OLEFIN ADDUCTS OF SULPHENYL HALIDES

T H E S I S

presented to the University of Glasgow

for the degree of M.Sc.

by

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1968

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J. H.

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INTRODUCTION

GENERAL

It was hoped that some problems which arise when working with olefins could be overcome by the preparation of suitable derivatives. For example, separation of a mixture of isomers which often co-occur in synthesis or in nature, is a long tedious process and not always possible, while the volatility of the compounds and their tendency to hydroperoxidise[1] add to the difficulties involved. A great advantage would be a general reagent to protect double bonds and characterise olefins by formation of adducts whose chemical and spectroscopic properties could be utilised in overcoming the fore-mentioned obstacles and from which the original olefins could be efficiently regenerated.

The best known derivatives are the dibromides,[2] of which many are crystalline compounds used in purification and for the protection of double bonds. For example, synthetic clovene(2) of high purity was obtained by formation of the dibromide and subsequent regeneration by treatment with zinc dust.[3]

An increasing number of π-complexes are being reported between unsaturated compounds and some transition metals, of which silver and platimum are the most important.[4,5]

These are finding application in chromatography[6] and as heavy atom derivatives for X-ray crystallography; for instance, the stereochemistry of humulene(3) was elucidated by an X-ray study of its silver nitrate adduct.[7]

Corey has described[8] a new stereospecific synthesis, especially useful for unstable alkenes, which involves formation of the diol, conversion to a thiocarbonate which decomposes on treatment with a trialkyl phosphite to yield the corresponding unsaturated compound. Cis(4) and trans(5) 1,4-diphenyl-2-butenes have been prepared from meso and racemic 1,4-diphenyl-2,3- butanediols; the hitherto unknown trans cyclooctene has been made by this method and trans cycloheptene detected by the formation of its 2,5-diphenyl-3,4-isobenzofuran adduct.

Other solid derivatives have been prepared by addition of iodine azide,[9] cyanogen azide[10] and sulphur dichloride.[11] Recently a considerable amount of research concerning sulphenyl halide adducts has been carried out and it is these compounds which have been selected for the following study.

SULPHENYL HALIDE ADDUCTS OF OLEFINS.

The stability of sulphenyl halides of general formula RSX, varies greatly depending on the nature of R and X.[12] The chlorides are more easily formed than bromides and iodides and for this reason the majority of sulphenyl halides which have been studied are chlorides.[13] Alkyl sulphenyl chlorides are unstable and therefore, are prepared as solutions at low temperatures immediately prior to use.[14] Those possessing no α-hydrogen atoms, for example trichloromethanesulphenyl chloride, have exceptional stability as chlorination of the α-carbon is impossible.[14] Most work concerning sulphenyl halides has been performed with aromatic compounds as these are more readily synthesised and are more stable.

The usual method of preparation is chlorinolysis, generally of the disulphide but thiols, thioesters and benzyl thioethers also react to give sulphenyl chlorides:-

$$RSSR + Cl_2 \longrightarrow 2\,RSCl,$$

$$RSH + Cl_2 \longrightarrow RSCl + HCl,$$

$$RSCH_2Ph + Cl_2 \longrightarrow RSCl + PhCH_2Cl.$$

In the case of aromatic compounds, the presence of electron donating substituents in the ring encourages a side reaction, electrophilic substitution, whereas electron withdrawing substituents protect the ring, favouring the

formation of stable sulphenyl chlorides.[15] The best known of these compounds is 2,4-dinitrobenzenesulphenyl chloride(1) whose properties and reactions have been studied by Kharasch.[16,17] The reasons for interest in this compound and for its selection for the following work are that it is easily prepared, is the most stable sulphenyl halide known and that it undergoes clean ionic reactions to give crystalline products in high yield. In addition sulphenyl chlorides liberate iodine from potassium iodide and therefore, the reactions can be followed by starch-iodide spot tests or accurately by titration with thiosulphate ($2\ ArS\ Cl + 2\ I^- \longrightarrow ArS\ S\ Ar + 2\ Cl^- + I_2$).[18,19]

Spectroscopic Properties of Olefin Adducts.

Although several lists of olefin adducts have been published,[18,20,21,22] there are few details of their spectroscopic properties in the literature.[23,24,25] Butler and Mueller[26] studying the mechanism of adduct formation, examined the proton magnetic resonance (p.m.r.) spectra of the adducts of acenaphthylene(6) and norbornene(7) with benzenesulphenyl chloride(8). The H-C-S and H-C-Cl proton signals appear separately in a clear region of the spectrum and their splitting patterns give information about the environment of the double bond.

Mass spectroscopy, which requires a microgram of

material, may be a useful tool in this field, the high molecular weight of the compounds being an advantage as low regions of spectrograms are difficult to discern. The elucidations of the breakdown patterns of halogen-containing molecules are simplified by characteristic isotopic abundances which make obvious the presence or absence of halogen in an ion created by electron impact. For example, chlorine has two common isotopes of molecular weight 35 and 37 with relative abundances in the ratio 3:1. Therefore an ion containing a chlorine atom will give rise to two peaks, two mass units apart and with intensities in the ratio 3:1.

Uses of Sulphenyl Halide Adducts.

Sulphenyl halide adducts have been used occasionally for characterisation purposes.[23,27,28] Kharasch when recommending this practice,[17,18] points out the spread of melting points of the adducts of similar olefins, even of cis and trans isomers.[23,27]

Reaction of sulphenyl bromides and iodides with many different types of compound would give heavy atom derivatives suitable for structure determination by X-ray crystallography. Some condensates, for example, those of alcohols, amines or ketones, do not contain the halogen atom but this difficulty could be surmounted by formation

of an adduct using an aromatic sulphenyl halide with bromine or iodine attached to the aromatic ring. Some such bromine substituted compounds have been reported[16] and though of low stability, used successfully in synthesis. Nitro- or dinitrobromobenzenesulphenyl chlorides may be more useful reagents for formation of X-ray derivatives as they should be of greater stability and more easily prepared due to the strong electron withdrawing nitro groups.

Sulphenyl halides[29] containing isotopically labelled sulphur or halogen can be prepared and used themselves or as their adducts in studies of reaction mechanisms. For example, the nucleophilic aromatic substitution reaction[30] of piperidine and phenyl 2,4-dinitrobenzene sulphone(9) has been studied using the latter compound enriched in the isotope S^{34}. An optically active sulphenyl halide[29] could also be prepared and used to resolve many types of racemate if suitable regeneration methods were available or could be found.

MECHANISM OF ADDITION OF SULPHENYL HALIDES TO OLEFINS.

Kharasch proposed that the reaction proceeds through a cyclic sulphonium ion, figure 1, and that stereospecific, trans, ionic addition occurs to give Markownikov products in glacial acetic acid.[18] The reaction is homogeneous[19] and peroxides, added to test the possibility of radical nature, oxidise the sulphenyl chlorides to sulphonyl chlorides leaving the direction of addition unchanged.[18] That no evidence of a free radical mechanism has been found is surprising as sulphide radicals are not uncommon, and are, for example, intermediates in the addition of mercaptans to double bonds[31] and it has been suggested[32] that a non-oxidising source of free radicals may initiate this process. Formation of adducts with geometric isomers of 2-phenyl-2-butene(10) and 2-butene(11)[23,33] gave in both cases, two different diastereomeric racemates which showed exclusive trans addition.[26] More recently a p.m.r. study of the coupling constants in the adducts(12),(13) of acenaphthylene(6) and norbornene(7) with benzenesulphenyl chloride(8), has confirmed the trans stereochemistry. Further proof for the above mechanism comes from kinetic studies[19,34,35] which show that the reaction in glacial acetic acid is first order in each reactant, second order overall; that the formation of the episulphonium ion is probably the rate-determining step; that addition of

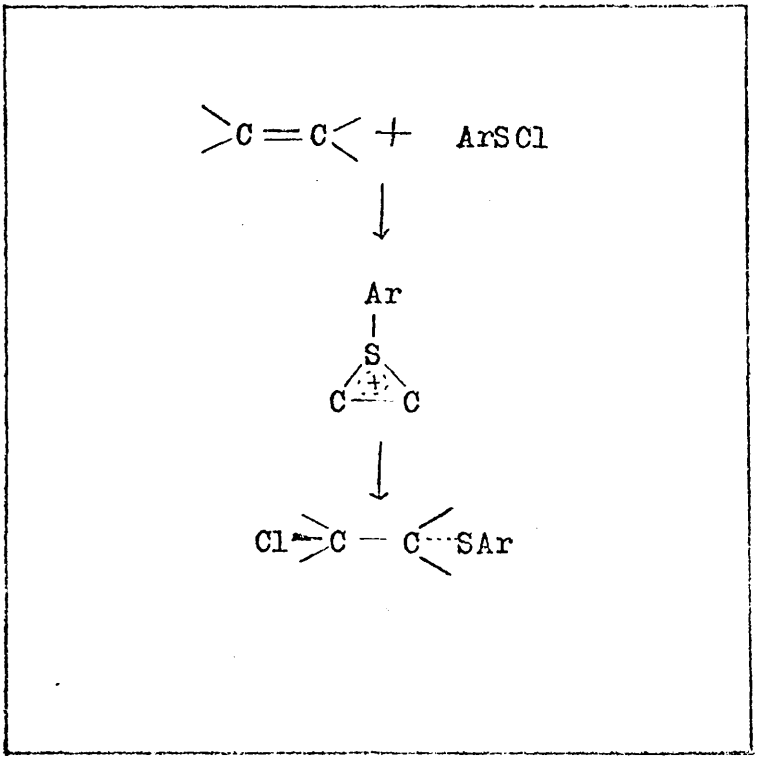


Figure 1.

Addition of (1) to a Double Bond.

lithium chloride or sodium perchlorate gives a positive salt effect.[19,35]

A rate study[36] of the reaction between para-substituted styrenes and (1) showed that the more nucleophilic the double bond, the more rapid addition occurred and the results were correlated by the Hammett relation. The rates of addition of (1) to 4-substituted cyclohexenes can be connected by Taft's equation,[37] indicating that the effect of the substituent is mainly electronic. The results for cis-4,5-disubstituted cyclohexenes were not in such good agreement but this can be explained as due to the unequal effects of axial and equatorial groups. The above data and that for a series of norbornenes also, are in accord showing that the rate of addition increases with the availability of electrons in the double bond. This is consistent with the fact that the one type of olefin which fails to react with (1),[18] is that substituted with electron withdrawing groups, for example, sorbic acid, acrylonitrile and tetrachloroethylene.

Solvents Effects.

Variation in solvent affects the rate of reaction, the more polar the solvent, the more rapid the reaction.[19,34] Kharasch pointed out[19] that the speed of the reaction in acetic acid may be partly due to acid catalysis, protonation

of the chlorine atom facilitating cleavage of the S - Cl bond. Campbell and Hogg[38,39] found for the addition of 2,4-dinitrobenzenesulphenyl bromide(14) to cyclohexene(15) in carbon tetrachloride, the order of the reaction greater than two and they suggested this being due to assisted solvation by the sulphenyl bromide in the transition state. This may also be the case for reactions of (1) in carbon tetrachloride and other solvents of low polarity as these have not yet been carefully investigated.

Orientation in Addition.

Kharasch[18] on adding (1) to propene(16) in glacial acetic acid, found the Markownikov product predominant but other workers[26] have reported anti-Markownikov products from the reactions of methyl-(17) and benzenesulphenyl chlorides(8) with several simple olefins in methylene chloride and the rearrangement of these on standing to give the expected Markownikov compounds. The adducts[24,40] of methylsulphenyl chloride(17) and vinyl acetylene(18) in methylene chloride are the source of more conflicting opinions. That the product obtained depends on both reactants and the solvent used and that either orientation is possible was concluded from a study of adducts[41] formed by addition of a variety of olefins to different sulphenyl halides in diverse solvents. The

ratio of normal norbornene adduct(19) to nortricyclyl 2,4-dinitrobenzene sulphide(20),[42] was also found to vary with the kind of solvent and purity of reagents used in the reaction.

In order to avoid these uncertainties and to have a good reaction rate, glacial acetic acid at room temperature was used throughout the present study and the only sulphenyl halide used was (1).

Anomalous Olefins Adducts.

A number of anomalous adducts have been reported and the mechanism of the normal electrophilic addition reaction can be extended to explain their formation. Elimination of a proton from the cyclic sulphonium ion gives rise to vinyl sulphides, the derivatives(24), (25), (26) of 1,1-diphenylethylene(21),[18] camphene(22)[18] and 4-methoxystyrene(23).[36] Evidence in favour of this mechanism comes from comparison of the rate of formation of the 4-methoxystyrene derivative(26) with the rate of loss of hydrogen chloride from the normal adduct(27) prepared under special conditions. The latter reaction being much slower, shows that the vinyl sulphide must be formed directly. At low temperatures trans-stilbene(28) reacts to give the expected β-chlorosulphide(29) but when the reaction occurs in refluxing acetic acid,[43] a phenyl

group migrates and the product is identical to the 1,1-diphenylethylene adduct(24).

When norbornene(7) is treated with (1) the episulphonium ion may be attacked by chloride on the endo-side or delocalisation of the adjacent σ-bond may occur, followed by loss of a proton to give 2-chloronorbornyl 2,4-dinitrobenzene sulphide(19) and nortricyclyl 2,4-dinitrobenzene sulphide(20) (figure 2).

A diadduct[18] was obtained from the diene limonene(30) and the monoadduct could also be prepared, depending on the quantity of (1) used.

One adduct, that of anethole(31) was found to have an exceptionally labile chlorine atom. The usual method of preparation gave the β-acetoxysulphide(32) and an inert solvent, for instance benzene or carbon tetrachloride, had to be used to obtain the normal derivative. The corresponding β-methoxy-(33) or β-ethoxysulphides(34) were obtained on attempted recrystallisation of the latter from methanol or ethanol respectively.[18]

In every case the unusual derivatives formed, were crystalline compounds as suitable for characterisation purposes as β-chlorosulphides.

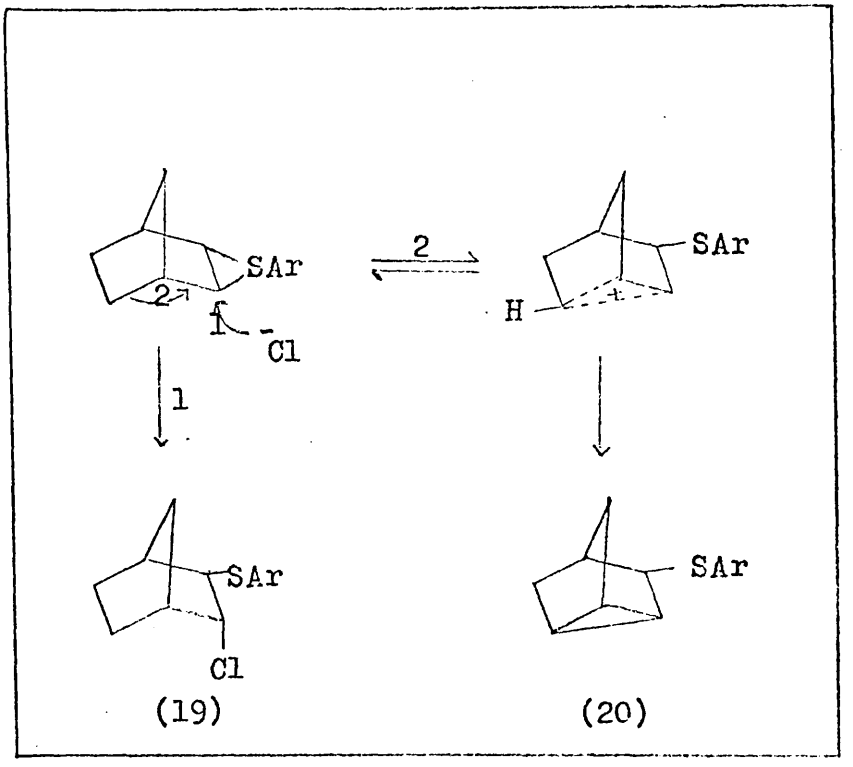


Figure 2.

Reaction of Norbornene with (1).

FURTHER REACTIONS OF β-CHLOROSULPHIDES.

The chemistry of β-chlorosulphides, with the exception of mustard gas, β,β'-dichloroethylsulphide,[44] has not been studied in great detail. They are known to hydrolyse rapidly,[45] react with base to give vinyl-sulphides,[46] may undergo substitution on reaction with amines[46] and potassium iodide[47] and oxidation to β-chloro-sulphoxides and β-chlorosulphones on reaction with various reagents.[47] The initial adducts can be converted to the β-chlorosulphoxides, β-chlorosulphones, the vinyl sulphides, sulphoxides or sulphones and various other similar compounds, all of which may have interesting spectroscopic properties.

When some of a series of adducts[23] of cis and trans 2-butene(11), were found to be liquids, they were oxidised to the corresponding sulphones which, with one exception, were crystalline compounds, useful for characterisation purposes. In order to prove their structures, adducts have been converted into known compounds by a series of reactions starting with oxidation to the sulphone and dehydrohalogenation.[18,19,48] Chlorinolysis of the norbornene adducts[42] in aqueous acetic acid gave anti-7-exo-2-dichloro-norbornane(35) and nortricyclyl chloride(36), known compounds, from which the structures of the adducts were

deduced.

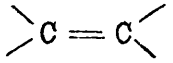
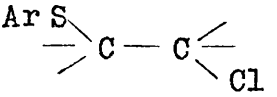
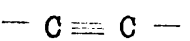
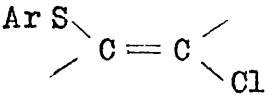
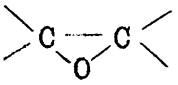
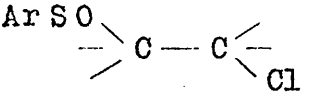
Possible synthetic uses exist for the β-chlorosulphides which can be modified as described above, the chlorine being substituted by a variety of nucleophiles and the sulphur group may be removed with Raney nickel. Reaction with pyridine gives a conjugated thiol in tautomeric equilibrium with the thione which can be hydrolysed to give a carbonyl compound.

OTHER REACTIONS OF ArSCl.

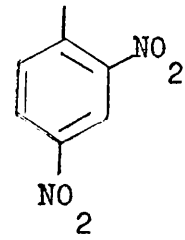
Sulphenyl halides are extremely versatile reagents and react with very different types of molecule, adding to unsaturated systems and substituting many other types of compound. In table 1, lists of the different reactants and of the products obtained, are given. While extending the range of compounds which (1) may be used to characterise, this complicates the situation for molecules containing more than one active functional group. The relative rates of reaction of these different groups and their interactions with respect to the addition of (1), are matters worthy of further examination.

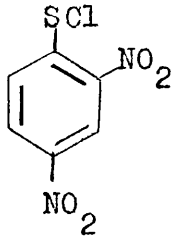
TABLE 1

Some Reactions of ArSCl

Reactants	Products
	
	
	
RNH_2, RNH_2	$RNHSAr$, $RNSAr_2$
$RCOH_3$	$RCOSAr_3$
RSH, Ar'SH	RSAr, Ar'SSAr
Ar'H	Ar'SAr
RCO_2Na	RCO_2SAr
R_2CHNO_2	R_2CNO_2 $\vert$ SAr
$RCOCH_3$	$RCOCHSAr_2$

In the following flow-sheets, Ar —





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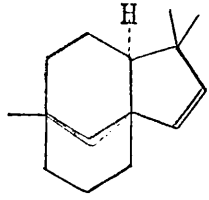

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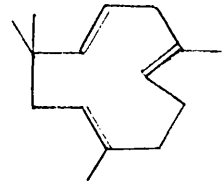

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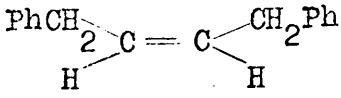

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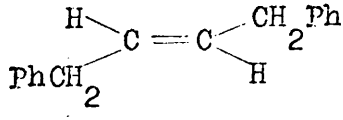

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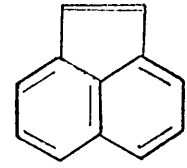

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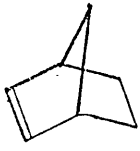

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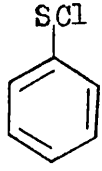

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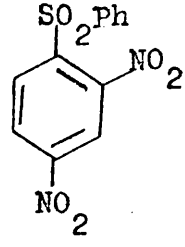

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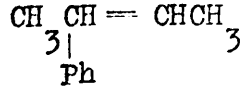

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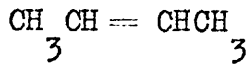

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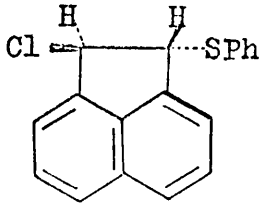

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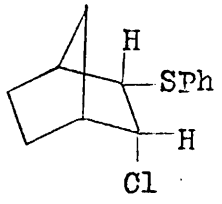

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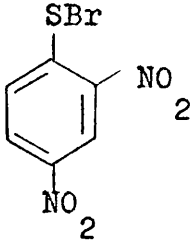

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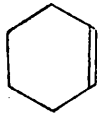

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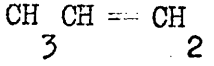

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MeSCl

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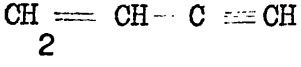

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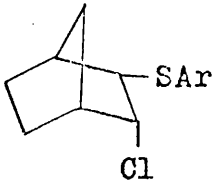

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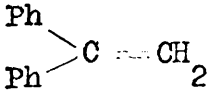

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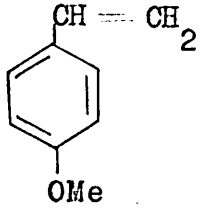

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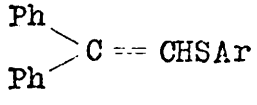

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The adducts of olefins with sulphenyl halides have already been proved useful for characterisation purposes.[27,28]

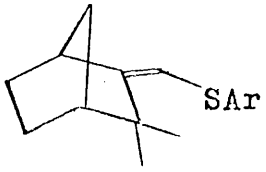
The various aspects of the present study as it was originally devised, were :-

(a) Investigation of the separation of mixtures of adducts by fractional crystallisation, by column, thin-layer and gas-liquid chromatography. Most adducts are highly coloured compounds which makes column and thin-layer chromatographic separation more easy to follow.

(b) A search for methods of regeneration of the olefins from the adducts. In studies of the reactions of halosulphides[47] with sodium and magnesium, one of the products obtained was ethylene and therefore the recovery of olefins from β-chlorosulphides seems plausible.

(c) Examination of the spectroscopic properties of the olefin adducts, particularly the p.m.r. and mass spectral, about which there is very little information presently available.

(d) A preliminary exploration of the further reactions of β-chlorosulphides and how these might be used as general synthetic methods.



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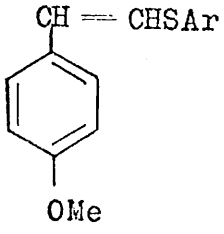

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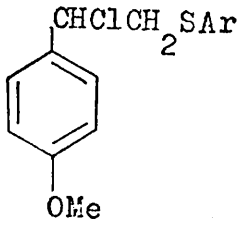

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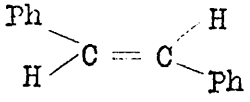

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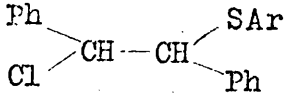

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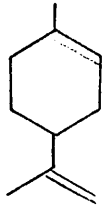

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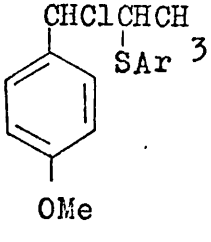

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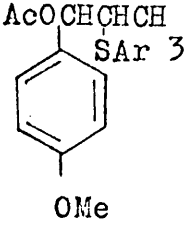

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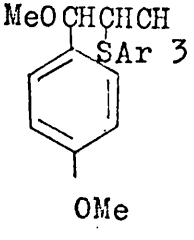

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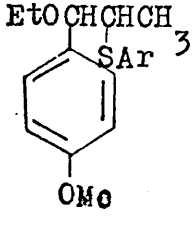

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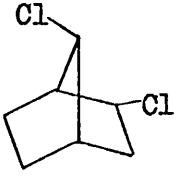

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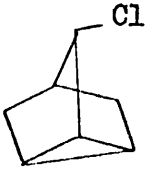

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DISCUSSION

CHAPTER 1

PREPARATION AND IDENTIFICATION OF THE ADDUCTS

Olefins

For the purposes of the present survey the cyclic monoolefins and dienes were either deliberately selected for study or became incidental to the study as it progressed. A few of the olefins used in the following work were synthesised but most were commercially available. 1-Methylcyclohexene(37), 1,2-dimethylcyclohexene(38) and 1,3-dimethylcyclohexene(39) were formed by treatment of cyclohexanone, 2-methylcyclohexanone and 3-methylcyclohexanone with Grignard reagent, methyl magnesium iodide, followed by dehydration with aluminium sulphate,[49] iodine[49] and potassium bisulphate[50] respectively. 1-Methylenecyclohexane(40) was prepared from triphenylmethylphosphonium bromide[51] and cyclohexanone by a Wittig reaction.[52]

The purity of the olefins was checked both by p.m.r. spectroscopy and by gas-liquid chromatography (g.l.c.) which showed the compounds obtained commercially to be about 99% pure. 1-Methylcyclohexene(37) was contaminated with 10% methylenecyclohexane(40), 1,2-dimethylcyclohexene(38) with approximately 20% 2,3-dimethylcyclohexene(41) and 5% 1-methylene-

2-methylcyclohexane(42). The latter mixture was distilled twice through a spinning band column and 1,2-dimethylcyclohexene(38) more than 95% pure resulted. The preparation of 1,3-dimethylcyclohexene(39) gave a mixture of the 1,3-(39) and 1,5-dimethylcyclohexenes(43) in the ratio 3:2 and separation proved impossible. From the Wittig reaction methylenecyclohexane(40), approximately 85% pure, was obtained.

Adducts(General)

The adducts were prepared by dissolving both reactants in acetic acid[18] at room temperature and the starch iodide spot test was used to show when all of (1) had reacted. The dienes were treated in the same manner, one or two equivalents of (1) being used to form the mono- or diadducts respectively. The crystalline products were removed by filtration, washed with solvent and recrystallised, a second crop being obtained by addition of ice to the filtrate and extraction with ethyl acetate. The adducts were recrystallised from a benzene-ethanol mixture as recommended by Kharasch[18] but some, for example the indene adduct(44), entrained ethanol which proved difficult to remove and therefore, to avoid this problem, another solvent system, methylene chloride-ether, was used.

Most derivatives were pure compounds which crystallised

without difficulty but a few, for example the cyclopentene (45) and acenaphthylene adducts(46), formed dark solutions which had to be clarified with animal charcoal. The yields from the pure olefins were high, the average being above 80%. The individual adducts were all highly crystalline and had sharp melting points, apart from the acenaphthylene derivative(46) which decomposed. A list of the whole series of adducts prepared, recording melting points, yields and analytical figures, appears in table 15 in the Experimental Section. Some adducts are described in detail in the following pages while others are referred to later in the appropriate contexts.

Attempts were made to record gas-liquid chromatograms on several different columns but with no success, decomposition occurring in every case. Thin-layer chromatography (t.l.c.) showed that the adducts of similar olefins had the same polarity which is not too surprising as the polar 2,4-dinitrobenzene group dominates adsorption and the hydrocarbon moieties are not sufficiently different to have much effect. This means that the separation of similar adducts is not practicable by any of the chromatographic techniques.

Most olefins reacted to give one pure compound, the Markownikov product in high yield according to the mechanism described in the Introduction. The p.m.r. spectra of the

material recovered from the mother liquors of the 1-methylcyclohexene(47) and 1-methylcyclopentene(48) adducts were examined for traces of an anti-Markownikov product which was found to be completely absent. Two compounds were formed on treatment of methylenecyclohexane(40) with (1), the expected adduct(49) in good yield and a small amount of 2-chloro-2-methylcyclohexyl 2,4-dinitrobenzene sulphide (47) showing that the olefin had undergone slight isomerisation in the acetic acid to form the more stable 1-methylcyclohexene(37).

From 1,2-Dimethylcyclohexene

In the first attempt to prepare a 1,2-dimethylcyclohexene adduct(50), the isomeric mixture of olefins was used, the reaction being carried out in the usual manner. When no crystals resulted, the solution was diluted with ice, extracted with ethyl acetate and solvent removal gave an orange oil which was shown to contain several compounds (t.l.c.). An infrared spectrum of the crude product showed in addition to the usual nitro and aromatic absorptions, a band at 1718cm^{-1} due to acetate. An unsuccessful attempt was made to separate the compounds on the basis of solubility differences. Chromatography on a silica column separated disulphide(51) from the rest of the mixture which was further chromatographed on an alumina column to give

three fractions. The first contained one compound (t.l.c.) which crystallised from a benzene-ethanol mixture. The p.m.r. spectrum revealed the characteristic pattern of a 1-(2,4-dinitro)benzene ring, two singlets at 5.02 and 5.18 τ which integrated for two protons, a singlet at 8.5 which integrated for three protons and eight methylenic protons between 7.4 - 8.8. Comparison of this with all the possible products identified the compound as 1-(2-methylcyclohexenyl) -methyl 2,4-dinitrobenzene sulphide(52). Supplementary evidence came from the infrared spectrum which had a weak absorption band at 1632cm^{-1} due to a tetrasubstituted double bond. The second fraction was a mixture with two components but the third crystallised to give 2,3-dimethyl-2-chlorocyclohexyl 2,4-dinitrobenzene sulphide(53) which was also identified by comparing all the possible structures with the p.m.r. spectrum. This showed the characteristic aromatic pattern, H-C-S a multiplet at 6.30τ, a methyl singlet at 8.43, a methyl doublet at 8.87 with a coupling constant of 7 cycles per second and six methylene protons between 7.7 - 9.0. Neither of these derivatives were formed from 1,2-dimethylcyclohexene(38) but from its isomers (42) and(41).

When the purified olefin(38) was reacted with (1) the product was an oil which decomposed during t.l.c. and

more slowly while standing at room temperature. A p.m.r. spectrum of this crude product showed the usual aromatic pattern, two methyl singlets at 8.17 and 8.60 τ, methylene protons between 7.7 - 8.4 and also visible, of less intensity five multiplets between 4.8 and 6.5. This indicated the presence of the expected adduct(50) which was not isolated pure, as it underwent slow decomposition or rearrangement.

From 3-Methylcyclohexene

Treatment of 3-methylcyclohexene(54) with (1) gave a crystalline product which melted over twenty-five degrees although t.l.c. in a variety of solvents indicated a pure compound. From the p.m.r. spectrum, table 2, it was obvious that two adducts were present and that these were the Markownikov(55)and anti-Markownikov(56) compounds formed by attack of the chloride ion on the episulphonium ion as shown in figure 3. 2-Chloro-3-methylcyclohexyl 2,4-dinitrobenzene sulphide(55) gave a doublet methyl at 8.88τ, H_b appeared at 6.30 as a multiplet coupled with two axial and one equatorial proton, H_a at 5.67 coupled with two axial protons, a quartet being broadened further by j_4 coupling and the characteristic pattern for a 1,2,4-substituted benzene ring was present. The anti-Markownikov product(56) had a doublet methyl at 9.01τ, H_b at 6.08, a quartet coupled with two axial protons, broadened by j_4

TABLE 2

P.m.r. of 3-Methylcyclohexene Adduct.

τ	Number of Protons	Coupling Constant(c/s)	Signal
1.02	1.4	3	d
1.57	1.4	10,3	q
2.39	1.4	10	d
5.67	1.0	4	q
5.84	0.4	-	m
6.08	0.4	4	q
6.30	1.0	-	m
8.88	3.0	7	d
9.01	1.2	7	d

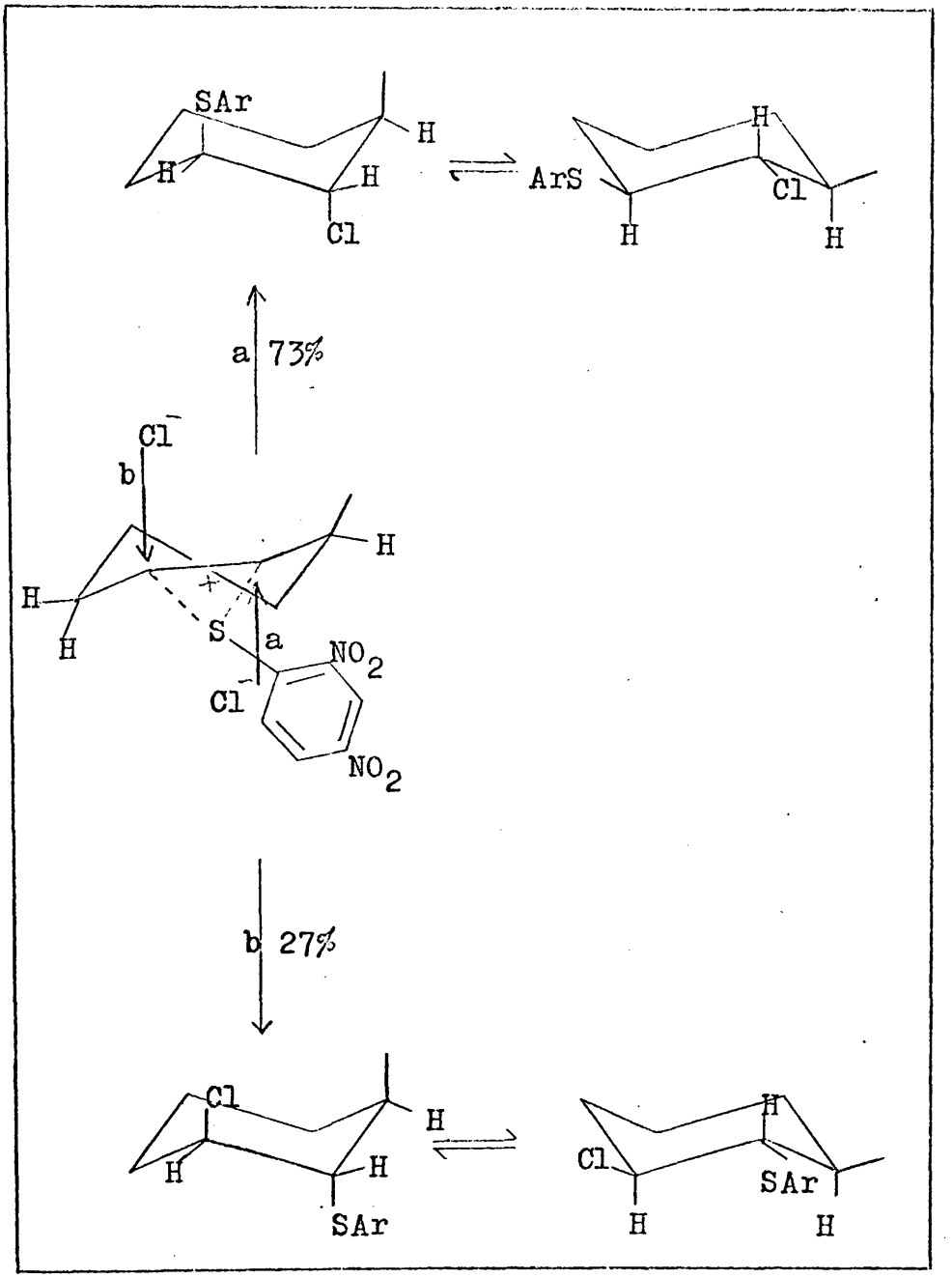


Figure 3

Reaction of 3-Methylcyclohexene with (1).

coupling, H_a at 5.84, a multiplet coupled with two axial and an equatorial proton and close examination of the aromatic region showed a small set of peaks partly hidden by those of the main compound.

The Markownikov adduct(55) was separated pure by fractional crystallisation in 52% yield and an attempt was made to separate the remainder by chromatography on an alumina column but very little pure material was obtained. Repeated preparative t.l.c. yielded a pure compound which was thought to be the anti-Markownikov product. Analytical t.l.c. indicated it was a new compound and the p.m.r. spectrum showed a doublet methyl at 8.80τ, multiplets at 6.00 and 6.78 integrating for one proton each, seven methylene protons between 7.4 and 8.5 and the usual aromatic pattern. It was thought that the original anti-Markownikov product(56) had rearranged on the silica and both the p.m.r. spectrum and the chemical analysis seem to indicate that the resultant compound is isomeric with the original, probably a more stable isomer.

From 1,3- and 1,5-Dimethylcyclohexene

It was hoped that the mixture of 1,3-(39) and 1,5-dimethyl-cyclohexenes(43) could be converted into a mixture of the corresponding adducts and the latter separated. The usual procedure gave an orange oil which contained four

compounds (t.l.c.). Fractional crystallisation and column chromatography both failed to isolate a pure compound but the separation of the two main products was acheived by repeated preparative t.l.c.. The p.m.r. spectrum of a mixture of the more polar compounds, present in 5% yield, showed that these were vinyl sulphides. The spectra of the other products both contained a singlet at 8.27 τ and a doublet at 9.01 with a coupling constant of 7 cycles per second, each of which integrated for three protons and the usual aromatic pattern. The one difference was in the signal due to the proton adjacent to sulphur which appeared as a multiplet for 2,4-dimethyl-2-chlorocyclohexyl 2,4-dinitrobenzene sulphide(58) at 6.08 τ and as a doublet at 6.45 τ slightly broadened by j^{4} coupling for 2,6-dimethyl-2-chlorocyclohexyl 2,4-dinitrobenzene sulphide(59).

From Cycloocta-1,5-diene

Cyclooctadiene(57) may react with (1) to form a normal monoadduct or the double bond may give rise to transannular reactions, probably by attacking the intermediate episulphonium ion; also, if two equivalents of (1) are used, diadducts may be formed. The possible mechanism and products are shown in figure 4. Treatment of the diene(57) with (1) gave an oil containing two compounds (t.l.c.) which were separated on an alumina column. The first

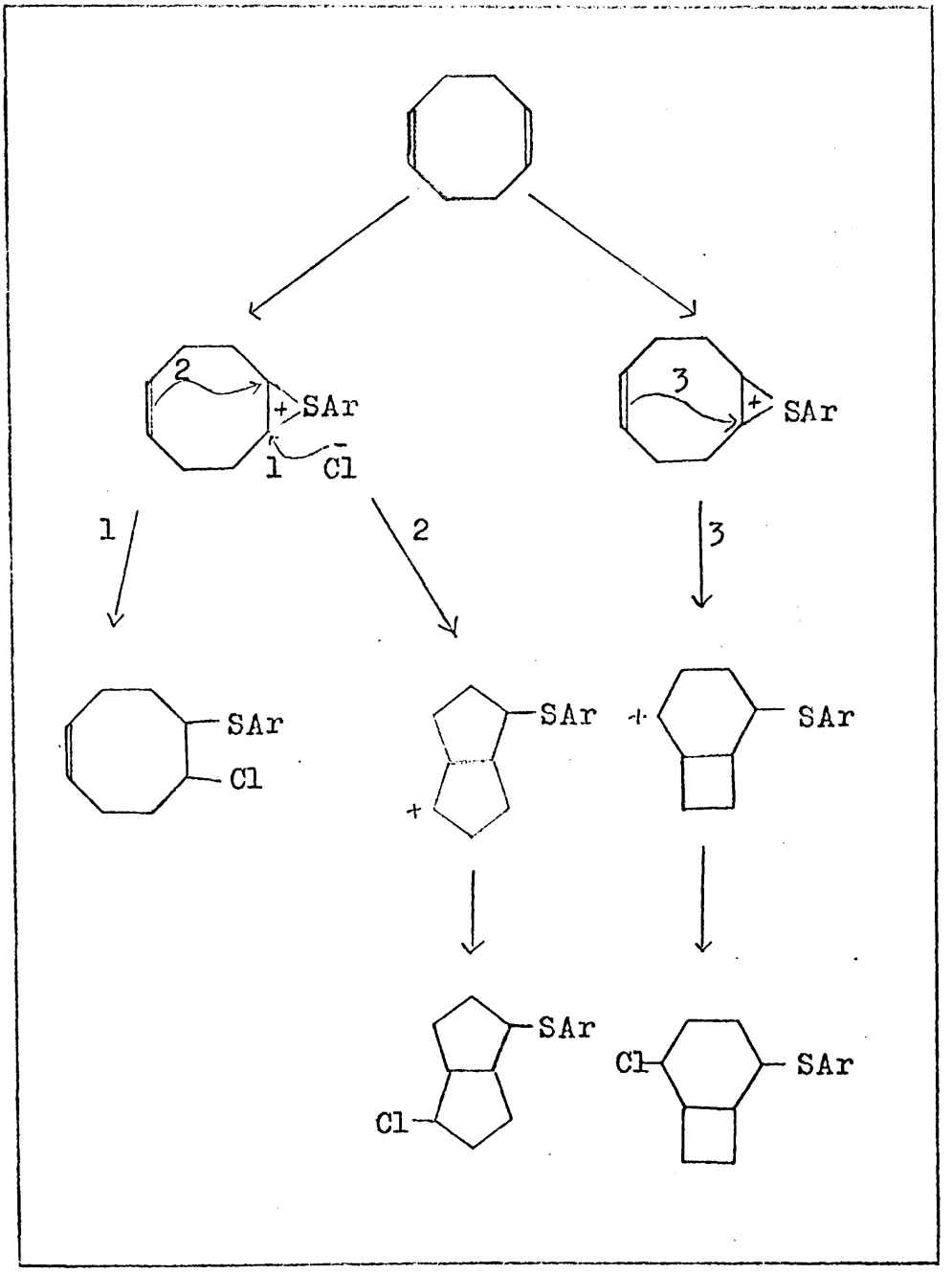


Figure 4

Reaction of Cyclooctadiene with (1).

crystallised and was identified as the simple monoadduct(60) from its p.m.r. spectrum which showed two vinyl protons, a multiplet at 4.25τ, two multiplets each integrating for one proton at 5.5 and 5.9, eight methylene protons between 7.1 and 8.5 and the usual aromatic pattern. The infrared spectrum had absorption bands at 1645cm^{-1} due to C=C stretch and 690cm^{-1} due to C-H deformation of a cis double bond which gave additional evidence for the structure (60). The second was isolated as an oil and this was later identified as a mixture of diadduct isomers by comparison with the products obtained from reaction of the diene(57) with two equivalents of (1). No trace of transannular products was found.

The diadduct formation afforded an oil and although t.l.c. showed one spot, it obviously consisted of an isomeric mixture. An attempt to dissolve the product in methylene chloride gave some insoluble solid material and a solution, from which on evaporation an oil was obtained which slowly solidified; neither solid was sharp melting. Two of the four possible isomers are shown in the flow-sheet, (61) and (62).

From Norbornadiene

Reaction of norbornadiene(63) with (1) may yield the usual monoadduct(64), a tricyclic adduct(65) or several

isomeric diadducts, for example (66), depending on the proportions of diene(63) and (1) reacted. When one equivalent was used, a pure compound crystallised from the reaction mixture and its p.m.r. spectrum showed a singlet at 5.96τ which integrated for two protons and was due to the H-C-S and H-C-Cl protons, two singlets at 7.59 and 8.10 both of which integrated for one proton, four more protons gave a series of peaks between 8.3 and 8.7, the usual aromatic pattern was present and a complete absence of vinyl protons indicated that both double bonds had been involved in the reaction. Analytical and mass spectrometric evidence ruled out the possibility of diadducts and this identified the product as the tricyclic compound(65).

Dilution of the mother liquors with ice and extraction with benzene gave two products which were separated by column chromatography. The more polar was the tricyclic compound (mixed melting point) and the other was identified as the monoadduct(64) from its p.m.r. spectrum which showed the aromatic protons at the expected values, two vinyl protons as a multiplet at 3.66τ, the H-C-S and H-C-Cl protons as a multiplet at 6.19, the two methine protons of C_1 and C_4 as a broad singlet at 6.76 and the methylene protons of C_7 as an AB quartet between 7.8 and 8.1 with

a coupling constant of 18 cycles per second. Supplementary evidence came from the infrared absorptions at 1640cm^{-1} and 690cm^{-1} characteristic of a cis double bond.

The reaction of norbornadiene(63) with p-toluenesulphenyl chloride(67) has been reported[53] as giving no nortricyclyl product. This can be explained on considering the intermediate sulphonium ions (68), (69) and (70). The inductive effect of the methyl group stabilises (68) as it tends to increase the electron density at the sulphur atom but (69) has two strongly withdrawing nitro groups which destabilise the classical ion and encourage double bond participation to give the non-classical ion(70) from which rearranged and normal products can arise.

It can be seen that little difficulty is involved in the preparation, purification and identification of these derivatives. Separation of a mixture by preparative t.l.c. exacts both time and patience and the incidental possibility of isomerisation cannot be excluded.

SPECTRAL PROPERTIES OF THE ADDUCTS

Infrared Spectra of the adducts are very similar as was expected. They are mainly useful in determining the presence of impurities such as ethanol or acetate and give evidence for double bonds in monoadducts of dienes and in vinyl sulphides. Taking as a typical example the cyclohexene adduct(71), the absorptions of which are listed in table 3 and the spectrum depicted in figure 5a, it can be seen that the dominant peaks are due to the aromatic part of the molecule, to the aromatic skeletal vibrations, to the asymmetric and symmetric stretch of the N - O bonds and to the C - N stretching vibration. Changing the substituents in the aliphatic part of the molecule causes no recognisable effect on these bands. There is a pattern for the various substituted aromatic rings to be found in the region 1200 - 600cm^{-1} arising from the C - H bending frequencies. The adducts all showed the same bands in this area and although these were different from the simple 1,2,4-trisubstituted aromatic rings, they were similar to those absorptions reported[54] for other 1-(2,4-dinitro)-benzene compounds.

The Ultraviolet Spectra of the adducts arise from the absorptions of the aromatic part of the molecules and

TABLE 3

Infrared Absorptions of the Cyclohexene Adduct.

CM^{-1}	Intensity	Vibration
3092	W	ν(C - H) aromatic
2940	M	ν(C - H) aliphatic
2858	M	ν(C - H) aliphatic
1593	S	C = C skeletal
1522	S	C = C skeletal, ν(N - O) asymmetric
1459	W	δ(C - H)
1450	W	δ(C - H)
1343	S	ν(N - O) symmetric
1052	M	ν(C - C)
919	W	δ(C - H)
832	M	ν(C - N)
744	W	δ(C - H)
734	M	δ(C - H)

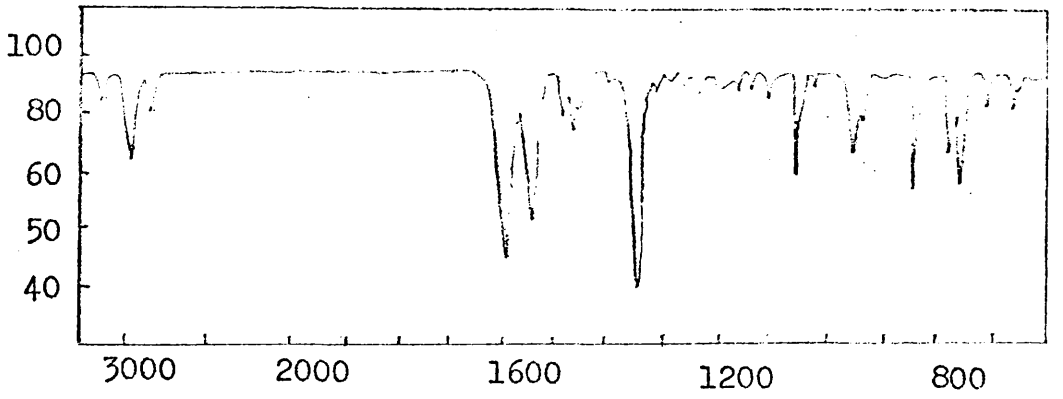


Figure 5a

Infrared Spectrum of the Cyclohexene Adduct.

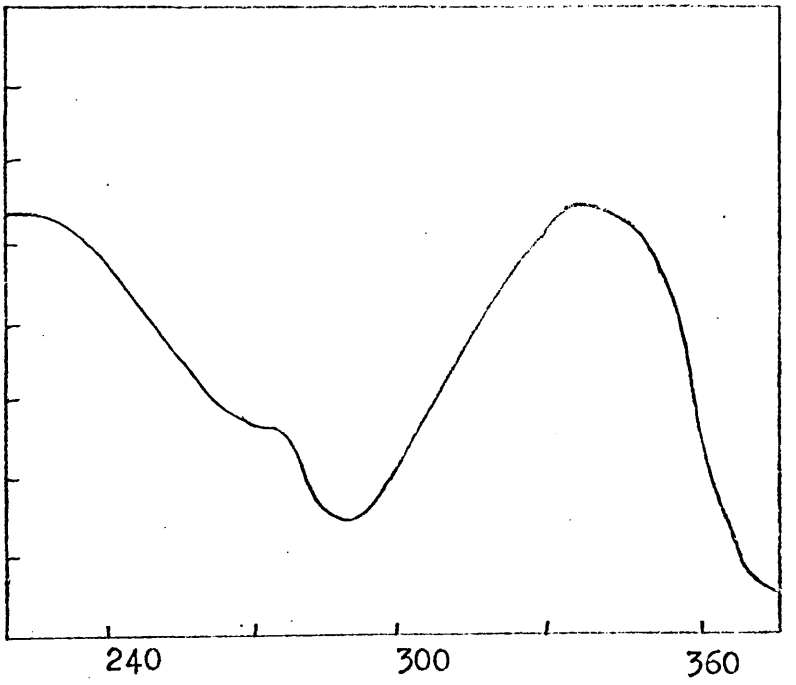


Figure 5b

Ultraviolet Spectrum of the Cyclohexene Adduct.

therefore one could anticipate their extreme similarity, illustrated in table 4 which records the electronic absorption spectra of a few derivatives.

Proton Magnetic Resonance Spectra were the most useful for structure elucidation and their use in identification of the derivatives of 1,2- (38), 1,3- (39) and 1,5-dimethylcyclohexenes(43), 3-methylcyclohexene(54), cyclooctadiene(57) and norbornadiene(63) has already been noted. The 2,4-dinitrobenzene group(72) gave rise to a characteristic pattern which was useful as an integration standard. At lowest field H_a appeared as a doublet (J-2cps.) at 1.06 τ coupling with H_b, H_b as a quartet (J-2,8cps.) at 1.64 due to ortho-coupling with H_c (J-8cps.) and meta coupling with H_a (J-2cps.), H_c as a doublet (J-8cps.) at 2.31 due to coupling with H_b. The p.m.r. spectra of the adducts have been tabulated in table 5 and it can be seen that H-C-Cl varied between 4.30 - 5.96 and H-C-S between 4.41 - 6.37.

The most interesting spectrum was that of the indene adduct(44), figure 6, which had a doublet (J-2cps.) at 4.56 τ, a doublet (J-8cps.) with fine structure at 5.46, a quartet (J-8,16cps.) at 5.90 and a doublet (J-16cps.) with fine structure at 6.74, all of which integrated for one proton. The four aromatic protons appeared as a singlet at 2.54 besides the usual pattern of the 2,4-

TABLE 4

Ultraviolet Absorption Spectra.

Adduct	λmax	λmin	λmax
cyclohexene	268 (6490)	288 (3390)	334.5 (12740)
1-methylcyclohexene	269 (6240)	289 (3630)	330 (12320)
3-methylcyclohexene	269 (6907)	287 (4176)	330 (12208)
cycloheptene	268.5 (5850)	288 (3240)	333 (11841)

TABLE 5

P.m.r. Spectra of the Adducts.

Adduct	H - C - Cl	H - C - S	CH_3 -	$-CH_2-$	Ar - H
cyclopentene	5.66 m	5.95 m		7.1 - 8.3	
cyclohexene	5.96 m	6.37 m		7.4 - 8.8	
cycloheptene	5.66 m	6.04 m		7.5 - 8.5	
cyclooctene	5.80 m	6.18 m		7.6 - 8.6	
1-methylcyclopentene		5.89 m	8.22 s	7.2 - 8.5	
1-methylcyclohexene		6.25 m	8.29 s	7.6 - 8.7	
3-methylcyclohexene	5.70 q 4cps	6.25 m	8.86 d 7cps	7.2 - 9.2	
2,3-dimethylcyclohexene		6.30 m	8.43 s 8.87 d 7cps	7.7 - 9.0	
methylenecyclohexane		6.46 s		7.7 - 8.5	
acenaphthylene	4.33 s	4.45 s			2.0 - 2.5
stilbene	4.82 d 7cps	5.15 d 7cps			2.88
indene	4.56 d 2cps	5.46 q 2,8cps		5.90 q 8,16cps 6.74 q 2,16cps	2.54

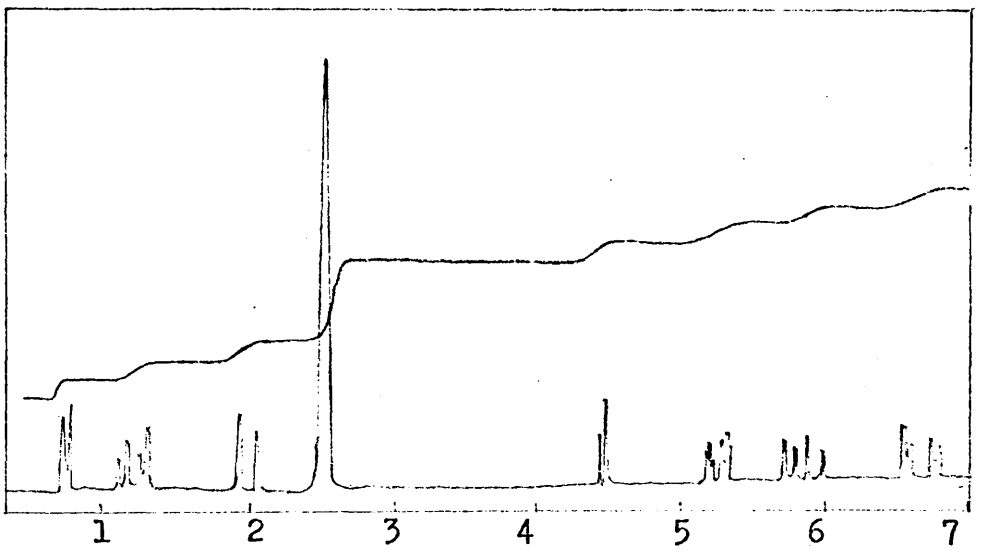


Figure 6.

P.m.r. Spectrum and Integration of Indene Adduct.

dinitrobenzene group. To explain the spectrum, it had to be assumed that the five-membered ring was in a conformation where H_{Cl} was almost at right angles to H_S and H_S at right angles to H_b hence the coupling between these protons was very small. The signal at 4.56τ is attributed to H_{Cl} and the coupling constant is small (2cps.); the doublet at 5.46 to H_S which is coupled with H_a (J-8cps.) and the fine structure of the doublet is due to slight coupling interactions with H_b and H_{Cl}; the quartet at 5.90 is assigned to H_b which is coupled with H_a (J-16cps.) and H_b (J-8cps.) and the doublet at 6.74 to H_b which is coupled with H_S (J-16cps.) and H_b (J-2cps.). Confirmation of this came from double decoupling experiments when each proton was irradiated in turn and the others examined. As could be predicted from above, irradiation of H_{Cl} sharpened the H_S doublet, of H_S gave H_{Cl} as a singlet and H_a and H_b as doublets with J-16cps.; irradiation of H_a gave H_b and H_b as broad singlets and of H_b gave H_a as a doublet (J-8cps.) and sharpened the H_S signal. Irradiation at 2.54 sharpened the H_{Cl}, H_a and H_b signals showing there was slight coupling interaction with the aromatic protons, 2 and 5.

The Mass Spectra of the simple adducts were remarkably consistent in their fragmentations as can be seen from

table 6. The molecular ions are of low abundance but are easily recognisable since they appear as characteristic doublets due to the chlorine isotopes. The base peaks dominate the entire spectra so that it was necessary to increase the sensitivity while running the upper region. The ion ($M.W._{olefin}$-1) is usually base peak, the one exception being the ion ($M.W._{olefin}$) for the acenaphthylene adduct (46) and the spectra below these ions are derived from their fragmentation.

The 1-methylcyclohexene adduct(47) is a typical example (figure 7) which has the parent doublet at m/e 330, 332; the base peak at m/e 95 and a tentative scheme has been drawn up (figure 8) to explain how the main ions could arise. The aromatic thiol group gives rise to important ions at m/e 200, 183, 137 and to ones of lesser intensity at m/e 170 and 167. Hydrogen chloride is eliminated from the chlorohydrocarbon fragment to accord the most abundant ion at m/e 95 and a metastable ion. A retro-Diels-Alder rearrangement may then occur to give the second largest peak in the spectrum or loss of methylene may follow, both of these breakdowns providing metastable ions, evidence that the correct assignment has been made. The ions at m/e 95 and 81 each lose four hydrogen atoms in two stages to form the stable tropyllium, m/e 91, and benzene, m/e 77, aromatic ring systems and again corroborative evidence

TABLE 6

Mass Spectra of the Adducts.

	% Relative Abundance												
Adduct	44	45	46	47	48	49	52	53	55	58	71	73	74
m/e													
388			0.9										
386			1.9										
351			0.7										
350			1.9										
349			6.2										
346								0.3		0.5			0.8
344								1.0		1.4			2.4
332				0.4		2.7			1.0			1.0	
330				1.4		7.8			2.7			3.2	
318					1.4						0.2		
316					3.9						0.6		
313	5.4												
308							4.5						
305			1.1										
304		1.4											
302		3.6											
294						1.2							
287			3.3										
259			2.0										
220	11												

TABLE 6 (cont.,)

% Relative Abundance													
Adduct	44	45	46	47	48	49	52	53	55	58	71	73	74
m/e													
200		18	2	6	4	16	5	2	8	3	8	12	9
189			10										
187			30										
184		4	8	2	2	12	1			2		2	3
183	13	11		4	3	16	7	2	3	3	2	3	5
170	1	2		0.5	0.5		3		2	1	0.5	1	1
167		0.2	20	0.5	0.5	8	0.2	0.5		0.6	0.5		
152			100										
151			21										
150			11										
147								2					3
145								6					9
139			13										
137	1	4	1	4	2	16	1	2	2	3	1	2	3
136		3	1	2	1	8			1			1	2
133				1.5		5			1				
131				4		15			3				
126			5										
122.5			3										
119					3						1		
117					10						3		

TABLE 6 (cont.,)

% Relative Abundance													
Adduct	44	45	46	47	48	49	52	53	55	58	71	73	74
m/e													
116	52												
115	100												
110							12	9		18			12
109							100	100		100		22	100
108							7			7			
106.5			2										
106		4											
105		4											
103	20	10						2					
96		1		17		98			10			12	
95			4	100		100	18	8	100	12		100	6
93						21	15			10			
91						15	12	4		9			
82					8	18					6		
81				10	100	38	21	12		15	100	19	15
79	7			7	10	36	15	4		12	6	12	
77			5	7		25	12	4		10			
75			4			20							
69										10			
67		100		23	10		39	25	38	46		94	61
53				17	12		12	10	10	12	8	19	9

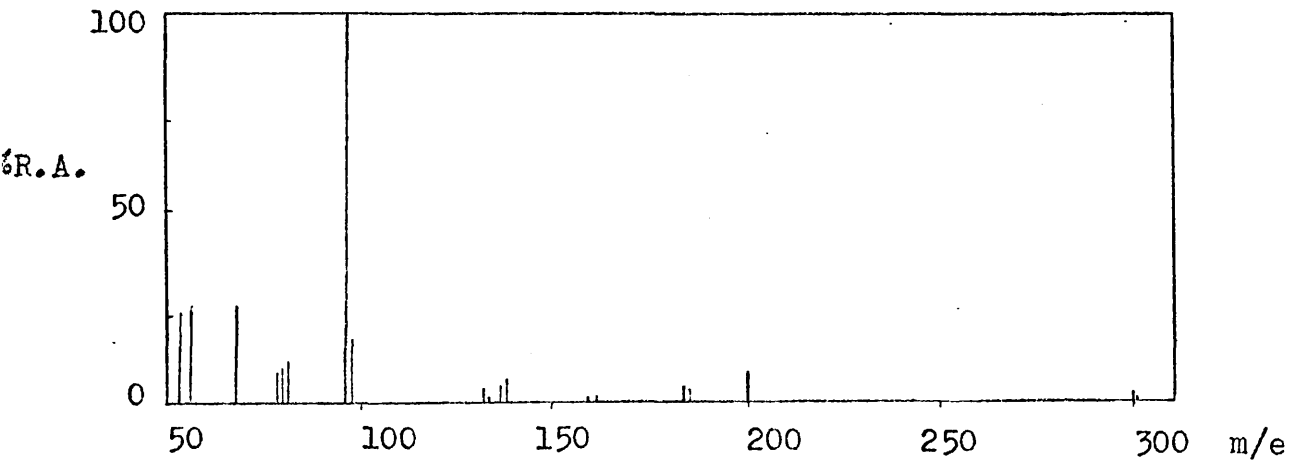
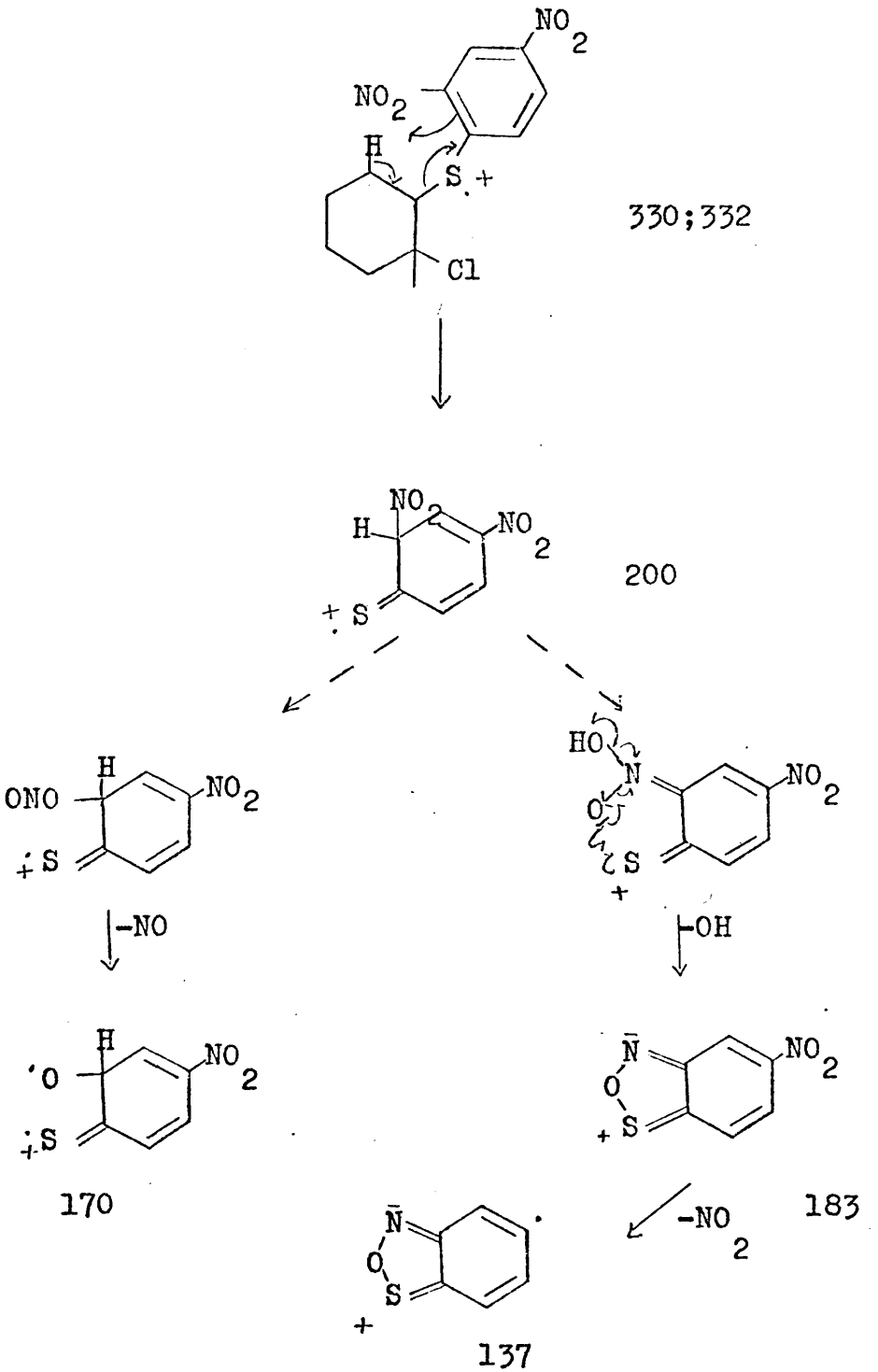


Figure 7.

Mass Spectrum of the 1-Methylcyclohexene Adduct.


330;332
200
170
183
137
-NO
-OH
-NO2

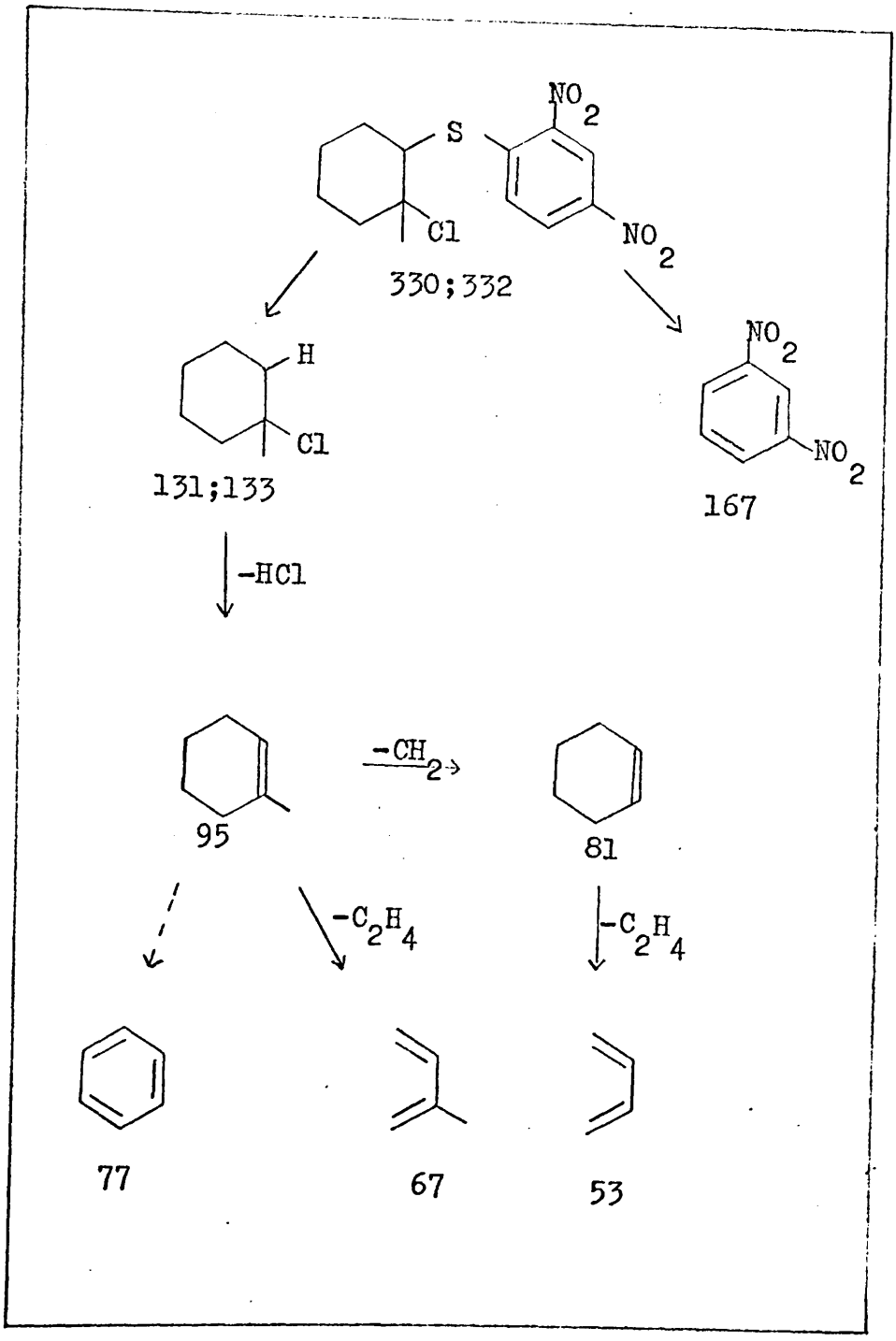


Figure 8.

Fragmentation of the 1-methylcyclohexene Adduct.

comes from four metastable ions. Table 7 records all the metastable peaks and the transitions from which they arise.

The mass spectra of the adducts all contain the mentioned aromatic thiol fragments, chlorohydrocarbon and hydrocarbon ions. The retro-Diels-Alder rearrangement seems to be very favourable for any six-membered ring while aromatisation will occur in any system which can acheive the required ring size either by breakdown or by rearrangement. The absence of the parent of the indene adduct(44) was noted, the ion of highest molecular weight being m/e 313 corresponding to loss of chlorine from the molecular ion. Both the indene(44) and acenaphthylene adducts(46) gave mass spectra characterised by ions of double charge which amounted to several percent of the base peak and the fragmentation of the hydrocarbons was more complex than in the case of the simple alicyclic ions.

The mass spectra of the diene adducts (60), (64) and (65), which are recorded in tables 8 and 9, show several main differences when compared to those of the simple adducts. The ions ($M.W._{olefin}-1$) do not dominate these spectra and only the norbornadiene adduct (64) has this as base peak. The aromatic thiol fragments at m/e 200, 183, 170, 167, 137 are also of less importance while the

TABLE 7

Metastable Ions of the 1-Methylcyclohexene Adduct.

Ions	Transitions			Calculated Value
91.3	95	⟶	93	91.5
89.2	93	⟶	91	89.1
77.3	81	⟶	79	77.2
75.2	79	⟶	77	75.1
69.2	95	⟶	81	69.6
68.9	131	⟶	95	68.9
47.3	95	⟶	67	47.4

TABLE 8

Mass Spectra of the Diene Adducts.

Adduct	60	64	65	Adduct	60	64	65
m/e				m/e			
344	1			145	9		
342	3			137	6		
328		3	2.5	129		11	
327	3			127		28	
326		10	6	107	6		
325	13			105	22		
314	2			95	10		
312	5			93	8		
307	4			92		16	10
298		1		91	30	100	26
296		3		81	18	9	9
291			4	79	100	9	8
262			1	77	16	9	8
260			3	75	40	9	13
200	4		1	66			98
183	4			65			100
177	19			55	17	19	13
175	52			53	23	7	
147	2						

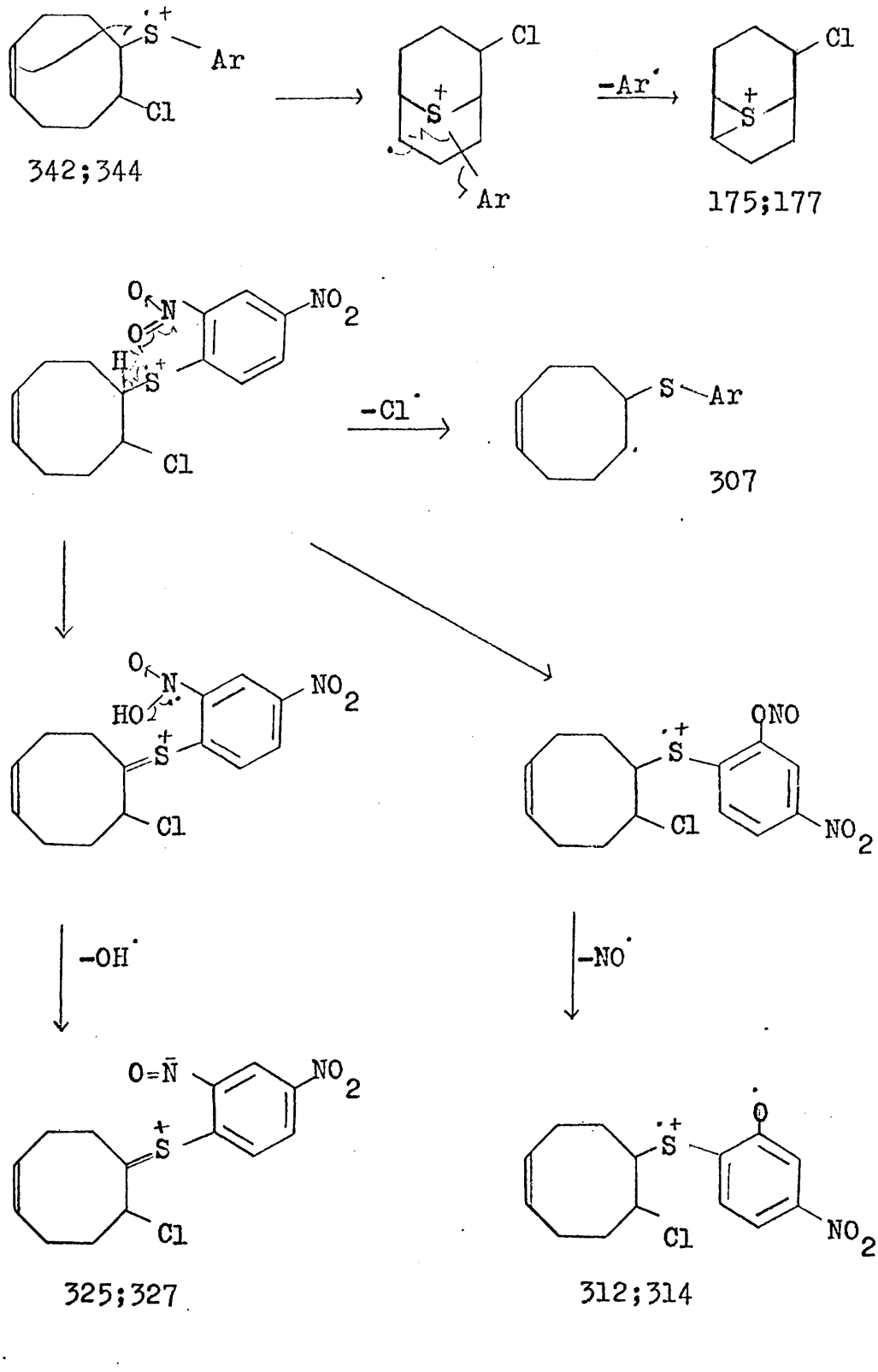
TABLE 9

Metastable Ions of the Diene Adducts.

Adduct	Ions	Transitions			Calculated Value
(60)	103.2	107	⟶	105	103.1
	90.6	342	⟶	175	90.3
	89.2	93	⟶	91	89.4
	77.4	81	⟶	79	77.3
	63.2	67	⟶	65	63.1
	58.5	107	⟶	79	58.4
(64)	77.4	81	⟶	79	77.3
	75.2	79	⟶	77	75.2
	64.6	127	⟶	91	64.5
	63.2	67	⟶	65	63.1
(65)	75.4	79	⟶	77	75.2
	47.6	91	⟶	66	47.8
	46.5	91	⟶	65	46.4

parent ions have a higher relative abundance as have ions due to loss of Cl, NO and OH which were much less than 1% in the spectra of the simple adducts.

The fragmentation of the cyclooctadiene adduct(60) is shown in figure 9. It was postulated that the double bond interacted with the sulphur atom leading to the ions at m/e 175, 177 and a metastable peak provides favourable evidence for this. The loss of NO from nitrocompounds has been reported[55] and is thought to involve rearrangement to the nitrite prior to fragmentation. A loss of OH is common in molecules containing ortho-nitro groups[56] and o-nitroaniline(75) can be cited as an example where rearrange-ment in a six-membered cyclic transition state affords loss of an OH radical. This is impossible in the case of the cyclooctadiene adduct(60) and it is necessary to assume the occurrence of hydrogen transfer wherein a very stable sulphonium ion is formed and subsequent fragmentation. The chlorohydrocarbon ion lost hydrogen chloride and the resultant fragment at m/e 107 isomerised to the conjugated form which gave the most abundant ion in the spectrum at m/e 79 via a retro-Diels-Alder rearrangement. The stable benzene and tropyllium ring systems were also formed and metastable peaks gave favourable evidence for most of the forementioned fragmentations.


342;344
-Ar·
175;177
-Cl·
307
-OH·
-NO·
325;327
312;314

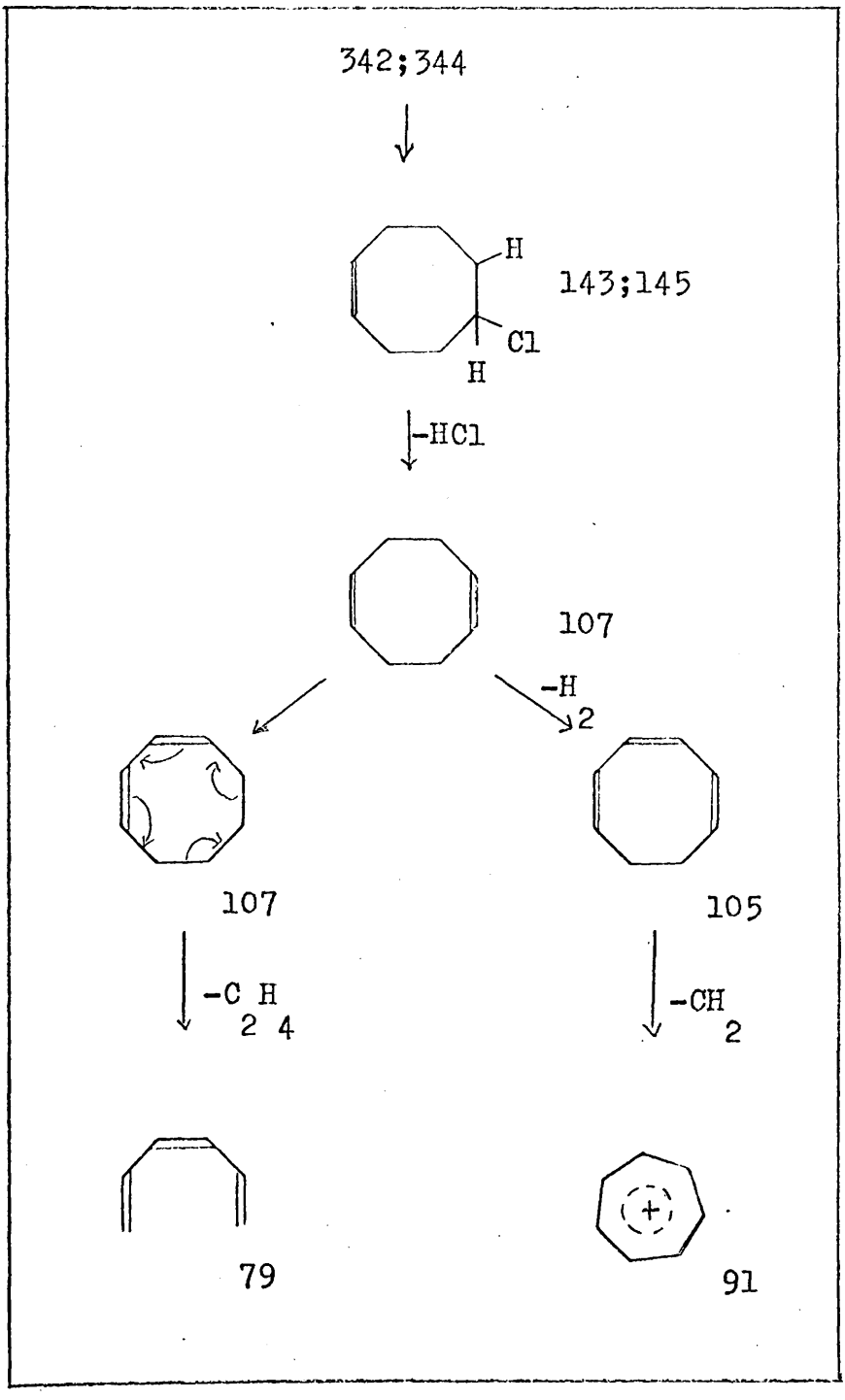
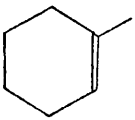


Figure 9

Fragmentation of the Cyclooctadiene Adduct.

Two surprising points were noted when comparing the mass spectra of the norbornadiene adducts. The normal derivative(64) had its most abundant ion at m/e 91, the ion ($M.W._{olefin}-1$) while in the spectrum of the tricyclic compound(65) this ion was only 26%, the base peak being that of cyclopentadiene at m/e 66. Although the usual adduct(64) contained a cyclohexene ring and might therefore be expected to undergo the retro-Diels-Alder rearrangement as shown in figure 10, no trace of this is apparent but the ions at m/e 260, 262 appear in the spectrum of the tricyclic adduct(65) which must first of all rearrange before decomposing in this manner.

It is obvious that valuble information about these adducts and the original olefins, can be obtained from the consideration of the various spectra, especially of the p.m.r. and mass spectra.



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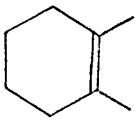

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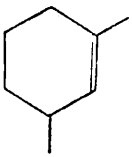

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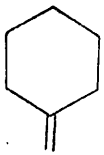

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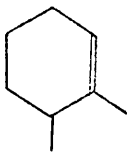

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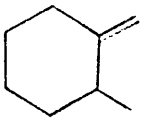

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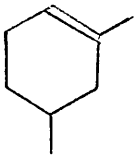

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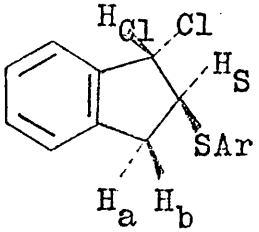

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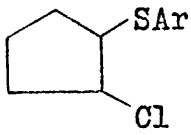

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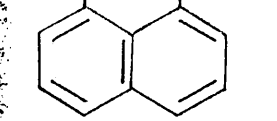

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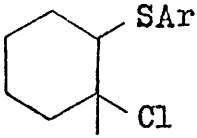

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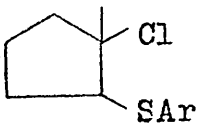

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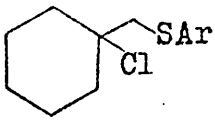

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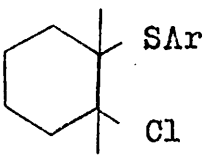

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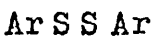

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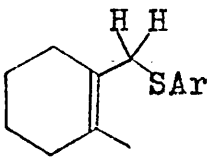

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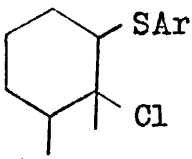

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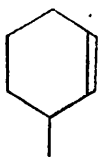

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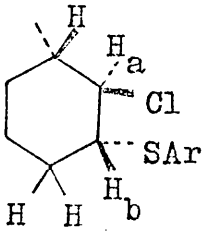

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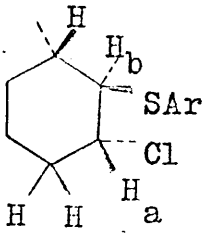

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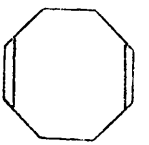

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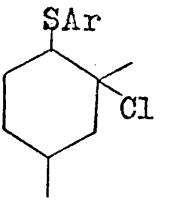

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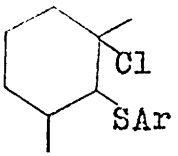

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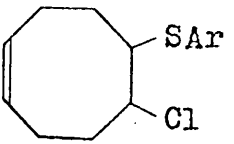

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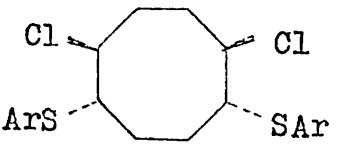

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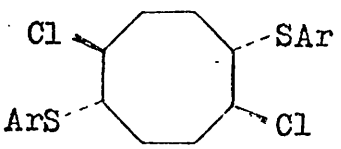

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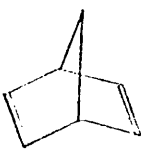

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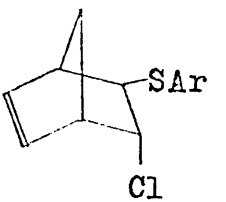

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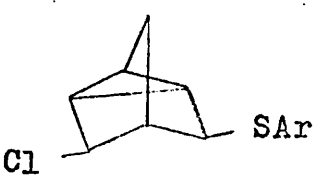

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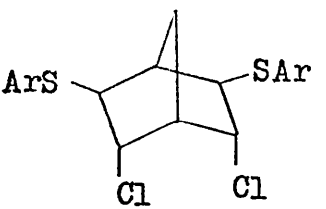

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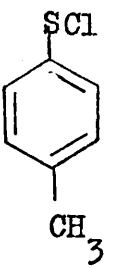

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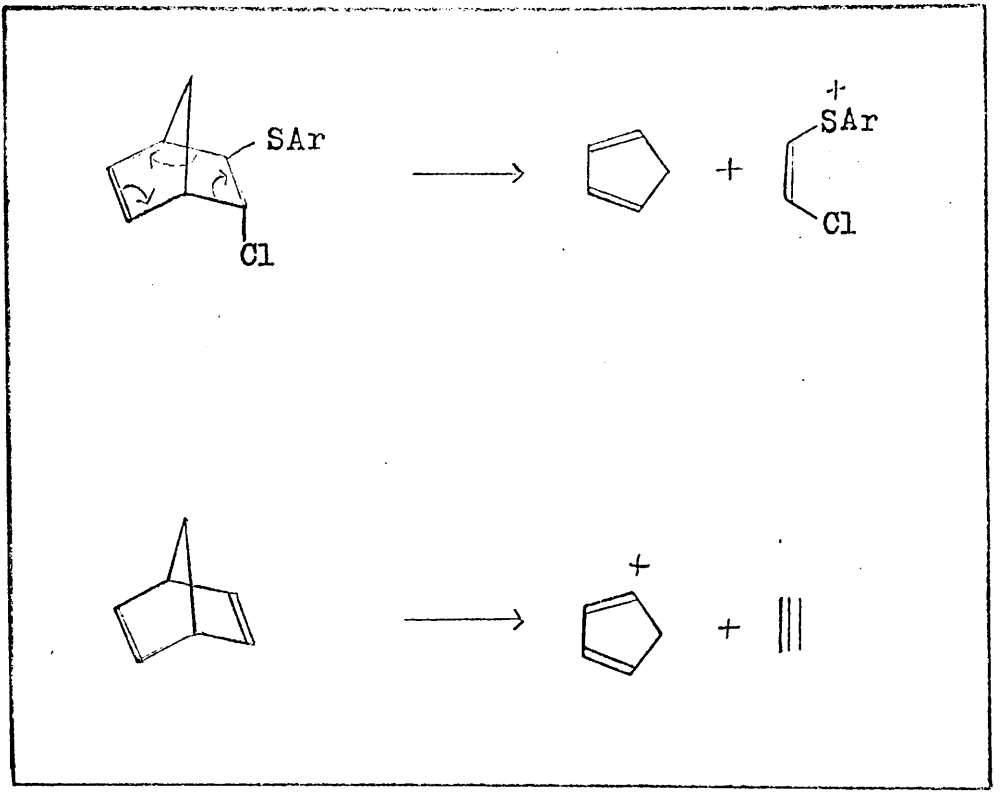
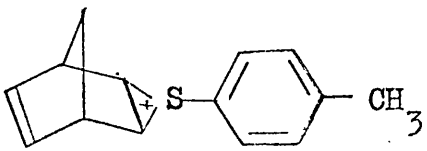


Figure 10

Retro-Diels-Alder Rearrangements.



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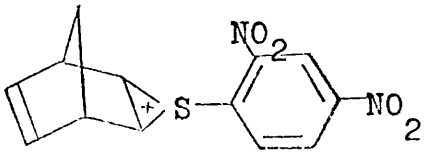

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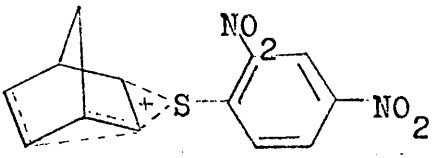

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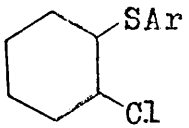

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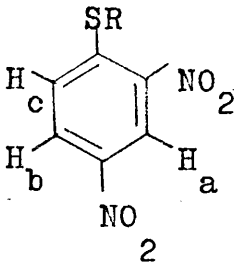

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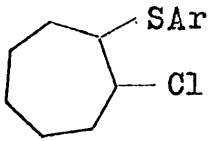

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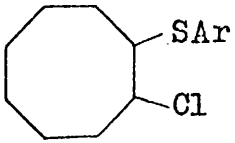

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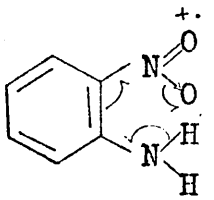

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CHAPTER 2

REGENERATION OF THE OLEFINS FROM THEIR ADDUCTS

The preliminary experiments were performed using β-chlorocyclohexyl 2,4-dinitrobenzene sulphide(71) and although g.l.c. showed the production of cyclohexene(15), its volatility and the fact that it co-distils with pentane (the extractant) hindered isolation of the pure olefin. It was necessary, therefore, to use the derivative of a less volatile olefin and the adduct of indene(44) was selected but proved unsuitable as indene(76) rapidly undergoes autoxidation. Thus the problems which it was hoped the preparation of derivatives would overcome, were becoming apparent in the regeneration experiments. It became clear that until an effective method of regeneration could be found and perfected it was desirable to avoid such difficulties by using a more tractable compound. The cyclooctene adduct(74) was finally recognised as the most amenable compound for this work.

It had been noted[47] that magnesium reacted with β-bromoethyl phenyl sulphide(77) to give ethylene, phenyl mercaptan and a disulphide. Despite the report that the corresponding chloro-compound was inactive, an attempt to regenerate the olefins from their adducts via an internal Grignard reaction was made here but initiation of the reaction

could not be acheived. It was hoped that this problem could be solved by using the entrainment method[57] which involves the continuous addition of a reactive auxiliary halide, such as ethylene dibromide, to keep the magnesium clean and active. The extra product formed is ethylene which escapes from the reaction mixture so that no separation problems result. This proved successful in that all the adduct decomposed but only a 30% yield of cyclooctene(78) was estimated by g.l.c. and it may be that the gaseous ethylene aids loss of the olefin.

It is well known[58] that bromides are more reactive Grignard reagents than the corresponding chlorides and it seems probable that substitution of the chlorine atom by bromine would enable a more successful regeneration by this method. If this is the case, recovery of the olefins from sulphenyl bromide adducts could carried out by this reaction.

Disulphides can be prepared by a large variety of methods,[59] they are the main product from hydrolysis of sulphenyl chlorides[60] and occur as by-products in many reactions. It seemed reasonable, therefore, that thiophenol or the thiophenolate anion might react with an adduct to form disulphides and that the corresponding olefin or chloro-olefin might be among the decomposition products. Heating the cyclooctene adduct(74) with thiophenol had little effect but when base was added the formation of disulphide(79)

and disappearance of adduct took place. The reaction mixture was extracted with pentane but g.l.c. of the concentrated extracts showed only a slight trace of cyclooctene(78).

Regeneration was next attempted by heating the adduct under reflux with sodium iodide in aqueous acetone or aqueous ethanol with interesting results. With acetone as solvent, t.l.c. showed the gradual disappearance of the adduct(74) and the formation of di-(2,4-dinitrobenzene)-disulphide(51) and another compound. When no adduct remained, after eight days, the reaction mixture was extracted with pentane and then with methylene chloride. A gas-liquid chromatogram of the pentane extract showed that cyclooctene(78) had been regenerated and gave an estimated yield of 23%. Preparative t.l.c. of the methylene chloride extract gave the new compound which had an infra-red absorption band at 1725cm^{-1} due to a C=O stretching vibration and its p.m.r. spectrum contained the usual aromatic pattern, a singlet at 6.10τ integrating for two protons arising from -S $\underline{CH}_2$ CO- and a singlet at 7.63 which integrated for three protons, corresponding to $\underline{CH}_3$ CO-. From this data it was concluded that the -SAr group had been transferred to the solvent to form acetonyl 2,4-dinitrobenzene sulphide(80), the acetone derivative.

Acetone was heated under reflux with (1) in glacial acetic to form the authentic derivative for comparative purposes and it was found to be identical in spectral and melting properties with(80).

When the acenaphthylene adduct(46) was treated in a similar fashion the olefin(6) was isolated pure in 82% yield and the acetone adduct(80) in 86% yield. However, no trace of cyclohexene(15) or any other compound containing the six-membered ring was found when the cyclohexene derivative(71) was reacted in this way although an 80% yield of acetone adduct(80) was obtained. Therefore it was concluded that regeneration had occurred but the prolonged heating process had enabled the volatile olefin to escape.

Repetition of the previous experiment using aqueous ethanol as solvent, gave very different results. From the adducts of cyclohexene(71) and 1-methylcyclohexene(47) no olefin resulted but t.l.c. revealed the presence of two products which were extracted with methylene chloride and separated by preparative t.l.c.. From the cyclohexene adduct(71), the more polar compound showed infrared absorption bands at 3450cm^{-1} and 1298cm^{-1} due to O-H and C-O stretching vibrations respectively. Its p.m.r. spectrum contained a multiplet at 6.53τ which integrated

for two protons and corresponded to the C<u>H</u>-S and C<u>H</u>-O systems; a sharp singlet at 7.71 which integrated for one proton and disappeared on the addition of deuterated water; the usual aromatic protons and the methylene envelope. The second compound had a strong infrared absorption band at 1091cm^{-1} due to a C-O stretching vibration and its p.m.r. spectrum showed signals which integrated for two protons at 6.39 τ, a quartet with J-7cps. corresponding to $CH_3\underline{CH}_2O$- and at 6.67, a multiplet due to the C<u>H</u>-S and C<u>H</u>-O systems. A three proton triplet appeared at 9.00 with J-7cps. corresponding to $\underline{CH}_3CH_2$- and the usual aromatic and methylene protons were also present. From this data the compounds were identified as β-hydroxycyclohexyl 2,4-dinitrobenzene sulphide(81) and β-ethoxycyclohexyl 2,4-dinitrobenzene sulphide(82) respectively. The 1-methyl-cyclohexene(47) derivative gave rise to the corresponding products (83) and (84) which were also identified from their infrared and p.m.r. spectra.

Under the same reaction conditions the cyclooctene adduct(74) and the acenaphthylene adduct(46) decomposed to give the corresponding olefins, (78) and (6), in 60% and 75% yield respectively. Comparative t.l.c. gave evidence that some substitution had occurred but these products amounted to less than 1% yield in both cases.

The most successful method of regeneration devised, involved treatment of an ethanolic solution of an adduct with zinc and a catalytic quantity of acetic acid, the reaction mixture being heated under reflux for several hours until all the adduct had decomposed (t.l.c.). After filtration the olefin was extracted with pentane and obtained pure by crystallisation or distillation of the extracts. Table 10 lists the olefins which were recovered, the percentage yields and methods of identification. The solid olefins were crystallised from the pentane extracts and were obtained in higher yield than the more volatile liquid compounds. Cyclooctene(78) was obtained pure from distillation of the extracts and treatment of the pentane distillate with (1) afforded more adduct(74) showing that a certain amount of olefin which was calculated, had co-distilled with the solvent. On the scale used, it was found impracticable to isolate compounds of greater volatility than cyclooctene(78) and the olefins were estimated either by treating the pentane distillates with (1) to form more adduct or by the g.l.c. technique described in the Experimental Section.

In order to determine if the reaction was stereospecific, the adducts(29) of cis(85) and trans(28) stilbene were prepared. Regeneration of these using this method gave

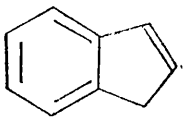
TABLE 10

Olefin Regeneration Using Zinc and Acetic Acid in Ethanol.

Olefin	Yield %	Estimation and Identification
cyclohexene	20	G.l.c. estimation. See Note 1, page 55. Isolated as adduct.
indene		Isolated by distillation. Infrared spectrum was similar to that of indene but with additional peaks due to hydroperoxidation products.
cyclooctene	48	Isolated pure and compared with an authentic sample in g.l.c. and infrared properties.
	73	
	25	Isolated as adduct from the pentane distillate.
cycloheptene	45	As cyclohexene.
1-methylcyclohexene	99	G.l.c. estimation.
acenaphthylene	85	Isolated pure and identified by a mixed m.p..
trans-stilbene	63	As cyclooctene.
cis-stilbene	59	As cyclooctene.

in both cases one compound, the starting olefin, the purity of which was checked by g.l.c. and by infrared spectroscopy. At least, therefore, in the case of the stilbenes, the regeneration was proved stereospecific.

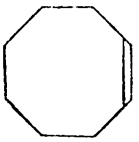
One of the previous methods may prove more successful for other olefins or adducts with different sulphenyl halides or some change in the reaction conditions may produce a further improvement. For example, it is likely that the Grignard reaction will prove efficient for the regeneration of sulphenyl bromide adducts but insufficient time existed for this investigation.



76

Br CH_2 CH_2 SPh

77



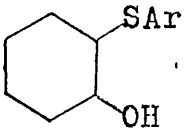
78

Ar S S Ph

79

CH_3 CO CH_2 SAr

80



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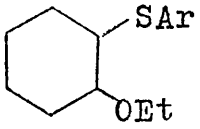

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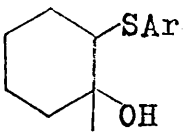

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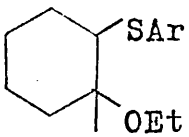

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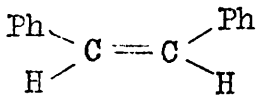

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CHAPTER 3

OXIDATION OF THE ADDUCTS

It had been hoped that time would be available to explore the chemistry of the adducts, substitution and elimination of the chloride and removal of the sulphur group for example, but it was only possible to study their oxidation reactions.

From the wide variety of ways in which sulphides can be converted to sulphoxides or sulphones, Cristol's method of oxidation[53] was selected first of all. The adducts were treated with a large excess of hydrogen peroxide in acetic acid, the reaction mixture being heated for half an hour, then left at room temperature overnight. When the crystalline product from the cyclohexene adduct(71), obtained on dilution with ice-water, was examined by t.l.c. it was found that two compounds were present and these were separated by preparative t.l.c. and identified by their infrared spectra. The less polar compound was colourless and showed strong absorptions at 1138cm^{-1} and 1323cm^{-1} characteristic of a sulphone(86) while the more polar, yellow compound absorbed at 1040cm^{-1}, a distinguishing feature of a sulphoxide(87). These assignments were verified both by the mass spectra and by chemical analyses.

When the cyclooctene adduct(74) reaction mixture was diluted with ice-water, no solid was obtained so the solution was extracted with ethyl acetate. After removing excess hydrogen peroxide by washing with ferrous sulphate solution, the solvent was evaporated and the residual oil examined on t.l.c. and found to contain many products, none of which were predominant.

Another method of oxidation[61] was attempted using exactly one or two equivalents of hydrogen peroxide in acetic acid and the solution being heated for fifteen or sixty minutes to form sulphoxide or sulphone respectively. The cyclohexene adduct(71) gave the desired products in high yield with this treatment but it was unsuccessful for the many other adducts tried, giving mixtures of many products. A procedure for obtaining sulphoxides using meta-chloroperbenzoic acid[62] was used for the cyclooctene adduct(74) but this also failed.

When the cyclopentene adduct(45) was dissolved in acetic acid and treated with aqueous potassium permanganate solution for two hours at room temperature, then decolourised with sulphur dioxide, a good yield of sulphone was obtained. When the experiment was repeated with the 1-(37) and 3-methylcyclohexenes(54), the reaction was much slower and required heating. The resultant sulphones (89) and (90)

were contaminated with small amounts of unreacted adduct and of sulphoxide, thus preparative t.l.c. was necessary to obtain the pure sulphones. The cyclooctene adduct(74) was also treated in this manner and the main product was the sulphoxide(92) although some sulphone(91) was also obtained. Table 16 in the Experimental Section shows the oxidation products, melting points, yields and analytical figures.

The sulphones are very stable compounds and have been used for characterisation purposes[23] when the initial adducts have been liquids. For example, the adducts of cis and trans butene(11) with 2-nitrobenzenesulphenyl(93), 2,4-dichlorobenzenesulphenyl(94) and p-toluenesulphenyl(67) chlorides were liquids but oxidation of these to the corresponding sulphones gave stable crystalline compounds.

SPECTRAL PROPERTIES OF THE OXIDATION PRODUCTS

The spectral properties of these compounds were examined in detail and compared with those of the initial adducts. Table 11 lists the main absorption bands for 2-chlorocyclohexyl 2,4-dinitrobenzene sulphoxide(87) and sulphone(86). The infrared spectra are very similar to those of the β-chlorosulphides but contain additional absorption bands, due to the S - O stretching vibrations. These bands appearing about 1040cm^{-1} for sulphoxides and about 1320cm^{-1} and 1130cm^{-1} due to the asymmetrical and symmetrical modes of vibration of the sulphone molecules, distinguish the two types of compound.

The ultraviolet spectra have been tabulated in table 12 showing the electronic absorption bands and their intensities. As in the case of the adducts, the sulphoxides and sulphones have almost identical spectra because the absorptions are due to the aromatic part of the molecule and little influenced by a change in the alkyl group.

The p.m.r. spectra were not distinct as those of the β-chlorosulphides. The protons adjacent to chlorine overlapped with those adjacent to the sulphoxide or sulphone groups so that each spectrum contained a multiplet which integrated for two protons around 6 τ. Table 13 lists the signals in the p.m.r. spectra of the oxidation products.

TABLE 11

Infrared Absorptions of the Cyclohexene Sulphoxide and Sulphone.

Sulphoxide cm^{-1}	Sulphone cm^{-1}	Intensity	Vibration
3096	3099	W	ν(C-H) aromatic
2940	2940	M	ν(C-H) aliphatic
2857	2859	M	ν(C-H) aliphatic
1600	1600	M	C=C skeletal
1550	1545	S	C=C skeletal
1538	1540	S	ν(N-O) asymmetric
1342	1344	S	ν(N-O) symmetric
--	1323	S	ν(S-O) asymmetric
--	1138	S	ν(S-O) symmetric
1093	1095	M	ν(C-C)
1040	--	S	ν(S-O)
909	910	M	δ(C-H)
829	831	M	ν(C-N)
758	758	M	δ(C-H)
740	740	M	δ(C-H)
725	726	M	δ(C-H)

TABLE 12

Ultraviolet Absorption Spectra of the Sulphoxides and Sulphones.

SULPHOXIDE	min	max	min	max
cyclohexene	195 (2720)	226 (19620)	320 (3550)	326 (3640)
cyclooctene	195 (3809)	226 (21620)	320 (4200)	326 (4640)
SULPHONE	**max**	**min**	**max**	**max**
cyclopentene	212 (14340)	221 (13480)	227 (14180)	293 (2340)
cyclohexene	209 (12510)	219 (9897)	237 (11000)	295 (1632)
cyclooctene	211 (10370)	224 (9645)	238 (10820)	294 (1413)
1-methylcyclohexene	209 (15950)	221 (14800)	237 (15050)	295 (2215)
3-methylcyclohexene	210 (11202)	220 (10200)	241 (11806)	295 (1410)

TABLE 13

P.m.r. Spectra of the Sulphoxides and Sulphones.

SULPHOXIDE	Ar-H	CH-S, CH-Cl	$-CH_2-$
cyclohexene	0.8 - 1.7	5.8	7.6 - 8.8
cyclooctene	0.8 - 1.7	6.7	7.4 - 8.9
SULPHONE			
cyclopentene	1.2 - 1.5	5.5	7.3 - 8.6
cyclohexene	1.2 - 1.5	5.7	7.4 - 8.8
cyclooctene	1.2 - 1.4	5.8	7.7 - 8.8
1-methylcyclohexene	1.2 - 1.5	5.3	7.6 - 8.6
3-methylcyclohexene	1.2 - 1.5	5.7	8.1 - 8.8

The signals from the aromatic protons also overlapped, more for the sulphones than for the sulphoxides thus each had a characteristic pattern in this region.

The mass spectra which were tabulated in table 14, were very similar to those of the β-chlorosulphides in the lower regions while in the upper part there are two main differences; the fragmentation of the oxythio-aromatic group and the greater intensity of ions arising from loss of small radicals from the molecular ion. In both the sulphoxide and sulphone spectra the ion ($M.W._{olefin}$-1) remained as base peak hence fragmentation below this again consisted of retro-Diels-Alder rearrangements where possible, aromatisation and loss of methyl or methylene radicals, most of these breakdowns giving rise to metastable ions. The chlorohydrocarbon ions were also present and in addition, there were, in the sulphone mass spectra, ions arising from cleavage of the S - Ar bond, for example, figure 11.

The mass spectra of 2-chlorocyclooctyl 2,4-dinitrobenzene sulphoxide(92) was unobtainable as thermal decomposition occurred at the temperature required to run the spectrum. The 2-chlorocyclohexyl 2,4-dinitrobenzene sulphoxide(87) gave no trouble and a satisfactory spectrum was acheived. The parent ion and chlorine isotope were less than 1% of the base peak and a P+1 ion and corresponding

TABLE 14

Mass Spectra of the Sulphoxide and Sulphones.

	% Relative Abundance					
Compound	87	86	88	89	90	91
m/e						
378						0.03
376						0.07
364				0.03	0.01	0.04
362				0.08	0.03	0.06
350		0.35				
348		1.00		0.05	0.02	0.20
346				0.14	0.07	0.50
335	0.06					
334	0.06	0.20	0.10	0.30	0.06	
333	0.2					
332	0.2	0.6	0.2	0.8	0.2	
320		1.0	0.3			
318	2.0	2.0	0.6			
316	7.0					
313		1.0				
310						1.2
296			0.8	1.2	0.8	
249	2.0					
233		11	4	1		

TABLE 14 (cont.,)

	% Relative Abundance					
Compound	87	86	88	89	90	91
m/e						
232		19	7	4	1	1
231		5	2	3	1	
216		4	2	2	1	1
215		16	8	4	2	2
200	8	2	2			
185		5	4	5	3	2
183	3	2				
170	2	6				
167		6				
152	22	18	6	4		5
145						4
143						6
133				12	4	
131				36	11	
119	8	36				
118	8	25				
117	22	95				
116	17	75				
110						14
109						100

TABLE 14 (cont.,)

Compound	% Relative Abundance					
	87	86	88	89	90	91
m/e						
105			12			
104			5			
103			48			
102			16			
96				71	17	7
95				100	100	7
93				4	9	7
91				30	7	7
82	58	99		7		9
81	100	100		76	9	19
79	64	99		60	11	15
77	36	72		50	9	8
75	50	98		52	12	11
68	5	8	47	36	7	11
67	51	20	100	71	26	69
65	17	37	46	23	7	9
63	16	13	20	23	6	7
55	33	98	9	71	21	26
53	62	99	16	70	13	17

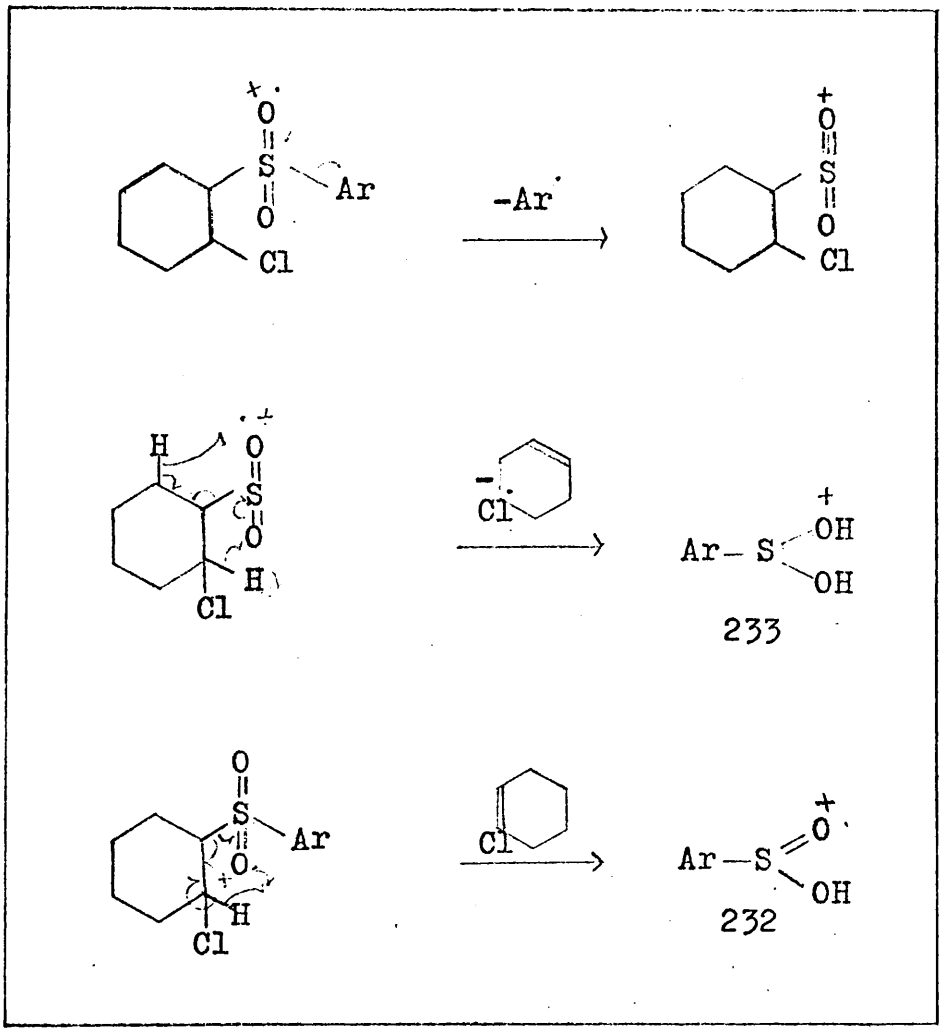


Figure 11

Fragmentations of the Sulphones.

chlorine isotope were also observed. An ion P+1 is formed by abstraction of a hydrogen atom from a neutral molecule by an ion in the source and this phenomenon is sometimes used to find the molecular weight when the molecular ion is very small.[66]

An ion, m/e 316, 318, corresponds to P - O and it seems likely the oxygen is lost from a nitro group rather than from the sulphoxide as no loss of oxygen from the latter has been reported. The other ion in this region is at m/e 249 which arises from loss of Cl and SO[67] from the parent ion. The main aromatic fragments are at m/e 215, 216 arising directly from cleavage of the S-alkyl bond and from rearrangement as shown in figure 12.

The sulphones have peaks due to loss from the molecular ion of 16, 30, 35, 60, 64, 65 and 66 varying in intensity between 0.5 - 10% due to loss of O, NO, Cl, 2NO, SO, SO_2H and SO_2H_2, the last three being a common characteristic of sulphones.[68] The aromatic group gives rise to ions at m/e 215, 216, 231, 232 and 233 corresponding to Ar SO, Ar SOH, $Ar SO_2$, $Ar SO_2H$ and $Ar SO_2H_2$, some of which are formed by simple cleavage while others involve single and double hydrogen rearrangements,[69] figure 11.

The p.m.r. signals of the initial adducts gave more information about both the adduct and the original olefin

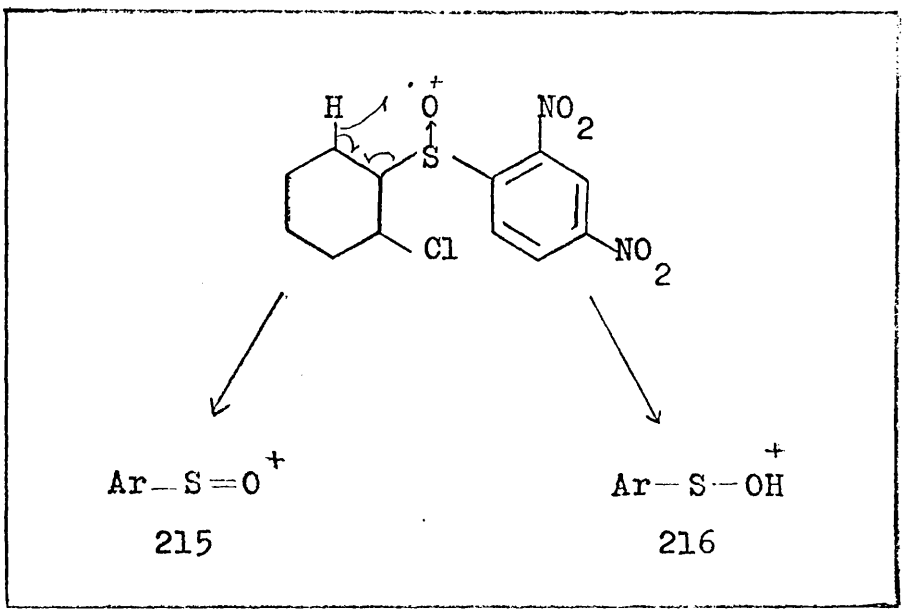
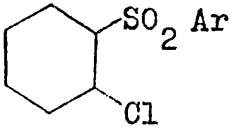


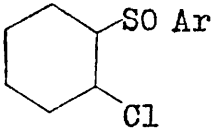
Figure 12

Fragmentations of the Sulphoxide.

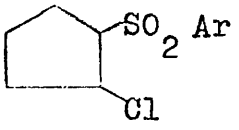
as the peaks due to the protons adjacent to sulphur and to chlorine were distinct. The oxidation products gave an interesting spectroscopic study and the mass spectra afforded similar information to those of the initial adducts although the p.m.r. spectra were not so advantageous.



86



87



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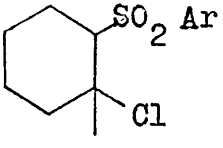
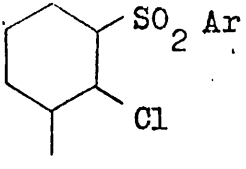
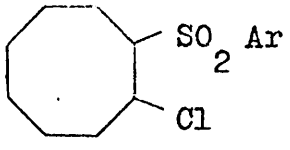


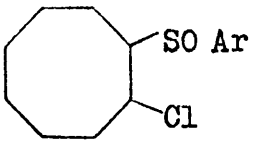
89



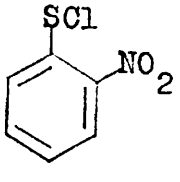
90



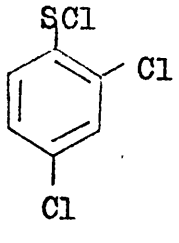
91



92



93



94

CONCLUSION

In most cases the adducts were very easy to prepare and purify and examination of their p.m.r. and mass spectral properties was a worthwhile process. The p.m.r. spectra gave evidence about the original double bond environment, other features such as methyl groups, cyclopropane rings, aromatic protons and were the means of identification of all the compounds. The mass spectra showed interesting fragmentation patterns and one could immediately obtain the olefin's molecular weight from the spectrum as the ion ($M.W._{olefin}-1$) or in one case the ion ($M.W._{olefin}$) had the greatest relative abundance. The mass spectra of the olefins are similar to the lower region of the adduct spectra but the latter are much easier to obtain, no problems arising from volatility as with olefins.

At first hopes of separation of mixtures of adducts were low as these had such similar polarities. While column chromatography was of little use, repeated preparative t.l.c. although a slow method was eventually successful in both cases where it was attempted. One compound isomerised during the separation process and this risk must always be considered.

One stereospecific regeneration method, treatment with zinc and acetic acid in ethanol, was found, by which the

olefin was recovered in good yield. Several other methods gave lower yields in most cases but perhaps these would be more successful for other compounds or could be further improved.

Insufficient time remained for a satisfactory study of the chemistry of the adducts. Some were oxidised successfully to the corresponding sulphoxides and sulphones, the spectroscopic properties of which proved to be of interest.

EXPERIMENTAL

Melting and decomposition points were determined on a Kofler hot-stage apparatus. Infrared spectra were recorded on a Perkin-Elmer 225 Grating Spectrophotometer of chloroform solutions with carbon disulphide solutions in the 1000 - 700cm^{-1} region in the case of the adducts and of potassium bromide discs for other compounds. P.m.r. spectra were run on the Perkin-Elmer R-10 spectrometer and those of the adducts and double decoupling experiments on the Varian Associates HA-100 spectrometer in deuterochloroform solution using approximately 0.3M solutions and with tetramethylsilane as internal standard. Mass spectra of the adducts were recorded on an A.E.I. MS9 mass spectrometer and of all other compounds on a A.E.I.-G.E.C. MS12 mass spectrometer. Electronic spectra were recorded on a Unicam SP 800A ultraviolet spectrophotometer.

G.l.c. was carried out on a Pye 'Argon Chromatograph' using a 25% Apiezon L column at 75° unless otherwise stated. Kieselgel G (Merck) was used for both analytical and preparative t.l.c.. After spraying with a solution of ceric ammonium sulphate(5g.) in concentrated sulphuric acid (50ml.) and diluted to 500ml., t.l.c. plates were warmed in an oven at 195° for approximately three minutes.

Light petroleum refers to the fraction b.p.(60 - 80)°.

Aqueous acetone and aqueous ethanol refer to mixtures of 80% solvent - 20% water.

Preparation of the 2,4-dinitrobenzenesulphenyl chloride adducts.

Typical procedure.

2,4-Dinitrobenzenesulphenyl chloride(1) and a slight excess of freshly purified olefin, were each dissolved in 'ANALAR' glacial acetic acid. The two solutions were mixed and allowed to stand at room temperature until a negative starch iodide test was obtained. Any solid product was removed by filtration and recrystallised. The filtrate was poured on ice, extracted with ethyl acetate, washed with brine, sodium bicarbonate and water, dried over anhydrous magnesium sulphate and evaporated to dryness. The product, oil or solid, was dissolved in methylene chloride and crystallised from a methylene chloride - ether mixture (1:1) to give pure adducts which usually melted over less than one degree centigrade.

Notes.

1. 2,4-Dinitrobenzenesulphenyl chloride(1) as supplied by Aldrich Chemical Co., Inc., contained approximately 40% disulphide(51). Recrystallisation from 'ANALAR' carbon

tetrachloride was necessary[18] and the purified reagent was stored in a refrigerator.

2. The purity of the olefins was checked by g.l.c. and by p.m.r. spectroscopy.

3. A benzene - ethanol (1:4) solvent system was used in some cases and the acenaphthylene adduct(46) was found to crystallise best from pure benzene. Certain adducts entrained ethanol during crystallisation and the latter was difficult to remove. The problem, in crystallising the indene adduct (44) for example, was overcome by using the methylene chloride - ether solvent combination.

4. The time for complete reaction varied between one minute and eighteen hours.

5. The reaction occurred more rapidly at higher temperatures but by-products were obtained except in very simple cases like the cyclohexene adduct(71) formation.

6. When darker, orange solutions of the adducts were obtained initially, these were clarified by treatment with animal charcoal prior to crystallisation.

7. When 1,2-dimethylcyclohexene(38) containing 20% 2,3-dimethylcyclohexene(41) and 5% 1-methylene-2-methylcyclohexane(42) was reacted with (1), two derivatives were isolated from the resultant oil by means of chromatography on a grade 1 alumina column. The product on treating

pure 1,2-dimethylcyclohexene(38) with (1) was an oil which decomposed slowly on standing.

8. 3-Methylcyclohexene(54) gave a mixture of Markownikov and anti-Markownikov products, (55) and (56) respectively, from which the former was isolated pure by fractional crystallisation. Little separation was acheived on a grade 1 alumina column but repeated preparative t.l.c. in 20% ethyl acetate - 80% light petroleum gave two pure compounds. The p.m.r. spectrum showed that the anti-Markownikov product(56) had isomerised on the silica.

9. The mixture of isomeric olefins, 1,3-dimethylcyclohexene (39) and 1,5-dimethylcyclohexene(43) gave a crystalline product containing four compounds (t.l.c.). Chromatography on a grade 1 alumina column failed to separate these but repeated preparative t.l.c. in 15% ethyl acetate - 85% light petroleum, gave the two main compounds, 2,4-dimethyl-2-chlorocyclohexyl 2,4-dinitrobenzene sulphide(58) and 2,6-dimethyl-2-chlorocyclohexyl 2,4-dinitrobenzene sulphide (59).

10. Cycloocta-1,5-diene(57) was treated with one equivalent of (1) in the same manner as the mono-olefins and the product was an oil containing two compounds (t.l.c.). Chromatography on a grade 1 alumina column separated the pure monoadduct(60) which crystallised from a benzene -

ethanol mixture and a small amount of diadduct. When two equivalents of (1) were used, the product was an oil from which a solid separated on attempting to dissolve it in methylene chloride. Evaporation of the solvent gave a second fraction, an oil which slowly solidified. The soluble fraction melted under 100 and the insoluble above 200 , both over a range of at least ten degrees.

11. Norbornadiene(63) reacted with one equivalent of (1) to give two compounds (t.l.c.), one of which partially crystallised from the reaction solution and the remainder was separated on a grade 1 alumina column to give the tricyclic adduct(65), identified from its p.m.r. and infrared spectra. The second compound was identified similarly as the mono-adduct(64). Both were crystallised from a benzene-ethanol mixture.

12. The yields, melting points (m.p.) and analytical figures are listed in table 15.

Notes (Table 15)

a. Yields recorded are those of the pure compound obtained.

b. Cis-stilbene adduct.

c. The reaction was still incomplete after seven days and the adduct formed was separated from the unreacted reagent by column chromatography.

d. Trans-stilbene adduct. e. Decomposition point (d.p.).

TABLE 15

ADDUCTS.

Adduct	M.p. °[b]	Yield %[a]	Microanalysis					
			Found			Calculated		
			C	H	N	C	H	N
29	153 - 154	45[c]	57.76	3.68	6.68	57.90	3.64	6.75
29	173 - 174[d]	42[c]	58.03	3.64	6.71	57.90	3.64	6.75
44	126 - 127	84	51.09	3.09	7.95	51.36	3.16	7.99
45	76 - 77	83	43.85	3.93	9.58	43.64	3.66	9.58
46	180 - 181[e]	72	56.08	2.59	7.35	55.89	2.87	7.24
47	144 - 145	86	47.46	4.76	8.36	47.20	4.57	8.46
48	107 - 108	90	45.40	4.27	9.00	45.50	4.14	8.84
49	134 - 135	78	47.36	4.76	8.34	47.20	4.57	8.46
53	128 - 129	20	48.79	4.94	8.27	48.76	4.96	8.12
55	162 - 163	52	47.44	4.53	8.65	47.20	4.57	8.46
56	114 - 115	16	47.31	4.57	8.41	47.20	4.57	8.46
58	99 - 100	36	48.93	5.02	8.35	48.76	4.96	8.12
59	115 - 116	25	48.76	5.04	7.97	48.76	4.96	8.12
60	131 - 132	61	49.09	4.63	8.07	49.05	4.41	8.14
64	134 - 135	18	47.82	3.51	8.73	47.78	3.39	8.57
65	172 - 173	78	47.77	3.37	8.49	47.78	3.39	8.57
71	119 - 120	86	45.72	4.25	9.01	45.50	4.14	8.84
73	151 - 152	85	47.33	4.62	8.56	47.20	4.57	8.46
70	141 - 142	88	48.56	5.20	8.19	48.76	4.97	8.12

Grignard reaction.

1. Dry magnesium (0.044g.) was covered with freshly distilled tetrahydrofuran (20ml.) and a solution of the cyclooctene adduct(74) (0.51g.) in tetrahydrofuran (20ml.) was added dropwise. Agitation with a glass rod, addition of iodine, methyl iodide, methyl magnesium iodide and mercury all failed to start the reaction and the adduct was recovered unchanged.

2. Dry magnesium (0.42g.) was covered with freshly distilled tetrahydrofuran (20ml.), the cyclooctene adduct(74) (0.51g.) in tetrahydrofuran (10ml.) added and the reaction mixture heated to 60°. A solution of ethylene dibromide (1.4ml. - 2g.) in tetrahydrofuran (20ml.) was added dropwise with stirring throughout the reaction. When no trace of adduct remained (t.l.c.), the solution was filtered, diluted with water and extracted with pentane (2X10ml.). The combined pentane extracts were dried over magnesium sulphate, then filtered and made up accurately to 25ml.. G.l.c. of a portion of this solution revealed that cyclooctene(78) (0.056g.) had been regenerated in 31% yield.

Notes.

1. Estimation of a small quantity of olefin by g.l.c..

To overcome loss by evaporation when small quantities or very volatile olefins were being utilised, a quantitative

g.l.c. technique was developed. The reaction mixtures were extracted with pentane and the extracts after drying, made up accurately to 25ml.. A known amount of this solution and a known amount of a standard solution were injected in turn, into the g.l.c. column, the areas under the resulting peaks being compared and hence the quantity of regenerated olefin calculated by proportion.

Treatment of the cyclooctene adduct with thiophenol.

The cyclooctene adduct(74) (0.42g.) was dissolved in ethanol (25ml.) and a solution of thiophenol (0.14ml.) in ethanol (25ml.) was added dropwise. The solution was heated under reflux for eighteen hours when the only change observed (t.l.c.) was the appearance of a slight amount of 2,4-dinitrobenzene phenyl disulphide(79) . A small quantity of pyridine (0.1ml.) in ethanol (5ml.) was added and the reaction mixture heated under reflux for a further forty - eight hours, by which time most of the adduct had decomposed and more disulphide(79) had formed (t.l.c.). The reaction mixture was extracted with pentane (2×5ml.) and the extracts dried over magnesium sulphate. G.l.c. of a portion of the pentane solution showed a very slight trace of material with the retention time of cyclooctene (78).

Treatment of adducts with sodium iodide in aqueous acetone.

1. The cyclooctene adduct(74) (0.40g.), sodium iodide (0.87g.) and aqueous acetone (25ml.) were heated under reflux for three days, by which time all the adduct had decomposed. T.l.c. in methylene chloride, of aliquots taken throughout the reaction showed the gradual disappearance of adduct and the formation of two new compounds. The reaction mixture was diluted with water, filtered, extracted with pentane (2×5ml.), the combined extracts washed with sodium thiosulphate, dried over magnesium sulphate and g.l.c. of the pentane extract showed the presence of cyclooctene(78) (0.038g.; 23%). In order to isolate and identify the new compounds, the aqueous layer was extracted with methylene chloride (2×5ml.) and the combined extracts washed and dried as above. Comparative t.l.c. showed the more polar compound to be disulphide(51). Preparative t.l.c. of the methylene chloride solution gave acetonyl 2,4-dinitrobenzene sulphide(80), the acetone derivative (0.13g.; 43%), m.p. 141 - 142°, mixed m.p. 141 - 142°, ν_{max}(nujol mull) 1725cm^{-1} (C=O). The p.m.r. spectrum showed a 2-proton singlet at 6.10τ corresponding to CO $C\underline{H}_2$ S and a 3-proton singlet at 7.63 corresponding to $C\underline{H}_3$ CO.

Analysis. Calculated for $C_9H_8N_2O_5S$: C, 42.18; H, 3.14; N, 10.93. Found C, 42.08; H, 3.11; N, 10.88.

2. The acenaphthylene adduct(46) (0.30g.), sodium iodide (2.5g.) and aqueous acetone (50ml.) were heated under reflux for eight days, aliquots of the reaction mixture being taken at intervals for t.l.c.. This showed the appearance of the olefin(6) and of the acetone condensate(80). When all the adduct had decomposed, the reaction mixture was extracted as above and preparative t.l.c. in 50% methylene chloride - 50% light petroleum gave acenaphthylene(6) (0.1g.; 82%), m.p. 92 - 93 and acetone derivative(80) (0.17g.; 86%), m.p. 141 - 142 .

3. The cyclohexene adduct(71) was treated as in 2. G.l.c. of the pentane extract revealed no trace of olefin though the acetone derivative (0.3g.; 86%) was obtained.

Treatment of adducts with sodium iodide in aqueous ethanol.

1. The cyclohexene adduct(71), sodium iodide (1.46g.) and aqueous ethanol (50ml.) were heated under reflux for three days, by which time no adduct remained (t.l.c.). The reaction mixture was diluted with water, extracted with pentane (2x10ml.) and then with methylene chloride (2x10ml.). Each extract was washed with sodium thiosulphate and dried over magnesium sulphate. G.l.c. of a portion of the pentane solution showed no trace of olefin. T.l.c. of the second extract in 20% light petroleum - 80% methylene chloride showed the presence of two compounds of Rf 0.15 and 0.52

which were compared to the ethanol adduct, Rf - 0.83, and found dissimilar. Preparative t.l.c. separated these two compounds and their structures were elucidated by p.m.r. spectroscopy. The more polar was β-hydroxycyclohexyl 2,4-dinitrobenzene sulphide(81) (0.46g.; 52%), m.p. 131 - 132°, ν_{max}^{KBr} 3450 (O - H), 1298cm^{-1} (C - O). The p.m.r. spectrum showed the usual aromatic pattern, a multiplet at 6.53τ which integrated for two protons due to the CH-S and CH-O systems and a sharp singlet at 7.71 which integrated for one proton and disappeared on addition of deuterated water, due to the OH proton.

Analysis. Calculated for $C_{12}H_{14}N_2O_5S$: C, 48.31; H, 4.73; N, 9.39. Found C, 48.53; H, 4.77; N, 9.48.

The second compound was β-ethoxycyclohexyl 2,4-dinitrobenzene sulphide(82) (0.19g.; 20%), m.p. 96 - 97°, ν_{max}^{KBr} 1091cm^{-1} (C - O). The p.m.r. spectrum showed a 2-proton quartet at 6.39τ (J - 7cps.) due to O CH_2 CH_3, a 2-proton multiplet at 6.67 which arose from the CH-S and CH-O systems and a 3-proton triplet at 9.00 corresponding to CH_3 CH_2.

Analysis. Calculated for $C_{14}H_{18}N_2O_5S$: C, 51.52; H, 5.55; N, 8.58. Found C, 51.48; H, 5.62; N, 8.68.

2. The 1-methylcyclohexene adduct(47) was treated as above and the corresponding products obtained and identified in the same manner. β-Hydroxy-β-methylcyclohexyl 2,4-dinitro-

benzene sulphide(83) (0.51g.; 60%), m.p. 92 - 93°, ν_{max}^{KBr} 3500 (O - H), 1296cm^{-1} (C - O), τ_{CDCl_3} 6.54 (m), 2H, C<u>H</u>-S and C<u>H</u>-O; 7.82 (s), 1H, O<u>H</u>; 8.60 (s), 3H, C<u>H</u>$_3$ C.

Analysis. Calculated for $C_{13}H_{16}N_2O_5S$: C, 49.98; H, 5.16; N, 8.96. Found C, 50.04; H, 5.18; N, 9.12.

β-Ethoxy-β-methylcyclohexyl 2,4-dinitrobenzene sulphide(84) (0.15g.; 19%), m.p. 96 - 97°, ν_{max}^{KBr} 1091cm^{-1} (C - O), τ_{CDCl_3} 5.70 (t), 1H, C<u>H</u>-S; 6.54 (q), J - 7cps., 2H, CH$_3$ C<u>H</u>$_2$ O; 8.67 (s), 3H, C<u>H</u>$_3$ C; 8.95 (t), J - 7cps., 3H, C<u>H</u>$_3$ CH$_2$.

Analysis. Calculated for $C_{15}H_{20}N_2O_5S$: C, 52.92; H, 5.92; N, 8.23. Found C, 53.21; H, 5.90; N, 8.39.

3. The cyclooctene adduct(74) (0.2g.), sodium iodide (0.25g.) and aqueous ethanol (50ml.) were heated under reflux for twenty-four hours, by which time all the adduct had disappeared (t.l.c.). The reaction mixture was diluted with water, extracted with pentane (2×10ml.), the combined extracts washed with sodium thiosulphate, dried over magnesium sulphate and made up accurately to 25ml.. The g.l.c. estimation gave cyclooctene(78) (0.043g.; 49%). The aqueous layer was then extracted with methylene chloride (2×5ml.), the extracts being washed and dried in the usual manner. T.l.c. of this solution showed compounds with Rf - 0.12 and 0.50, probably the hydroxy and ethoxy compounds but these amounted to less than 1%.

4. The acenaphthylene adduct(46) (0.17g.), sodium iodide (2.5g.) and aqueous ethanol (50ml.) were heated under reflux for eight days. The reaction mixture was diluted with water and extracted as above. Preparative t.l.c. gave acenaphthylene(6) (0.041g.; 75%). The substituted products were detected by t.l.c. but again constituted less than 1% of the total yield.

Preparation of the acetone derivative.

Acetone (2.1g.), 2,4-dinitrobenzenesulphenyl chloride (1) (1.98g.) and 'ANALAR' glacial acetic acid (20ml.) were heated under reflux for one hour. On dilution with water, a mass of dark crystals separated from the solution. These were clarified with animal charcoal and crystallised from ethanol to give the acetone derivative(80) (2.13g.; 85%), m.p. 141 - 142°, ν_{max}(nujol mull) 1725cm^{-1} (C=O), τ_{CDCl_3} 6.10 (s), 2H, CO C$\underline{H}_2$ S; 7.63 (s), 3H, C$\underline{H}_3$ CO. Analysis. Calculated for $C_9H_8N_2O_5S$: C, 42.18; H, 3.14; N, 10.93. Found C, 42.08; H, 3.11; N, 10.88.

Preparation of the ethanol derivative.

Ethanol (0.98g.), 2,4-dinitrobenzenesulphenyl chloride (1) (0.92g.) and pyridine (0.5ml.) were dissolved in ethylene chloride (15ml.). When the reaction was complete (starch

iodide test), the crystalline solid was removed by filtration, clarified by treatment with animal charcoal and crystallised from hot ethanol to give the ethanol derivative (1.03g.; 84%), m.p. 124 - 125°, τ_{CDCl_3} 5.92 (q), J - 7cps., 2H, $CH_3\underline{CH}_2O$; 8.43 (t), J - 7cps., 3H, $\underline{CH}_3CH_2$.

Analysis. Calculated for $C_8H_8N_2O_5S$: C, 39.34; H, 3.30; N, 11.47. Found C, 39.49; H, 3.26; N, 11.57.

Treatment of adduct with zinc and acetic acid in ethanol.

The cyclooctene adduct(74) (3.64g.), zinc(8.3g.), acetic acid (5ml.) and ethanol (200ml.) were heated under reflux for three hours, by which time t.l.c. showed the disappearance of all the adduct. The reaction mixture was filtered with suction through Celite 535, the filtrate extracted with pentane (3×25ml.), the combined extracts dried over magnesium sulphate, clarified with animal charcoal and concentrated by slow evaporation of solvent via a Vigreux column. Fractional distillation of the residue afforded cyclooctene(78) (0.53g.; 48%), boiling point 136 - 140°, identified by comparison with an authentic sample in infrared and g.l.c. properties. The pentane distillate was treated with (1) (1.22g.) in acetic acid (10ml.) and cyclooctene adduct(74) (0.93g.), m.p. 141 - 142° was obtained, equivalent to olefin (o.31g.) having co-distilled with the pentane.

This brings the total yield of cyclooctene(78) regenerated from the adduct to 73%.

Notes.

1. The optimum conditions, given above, were found after a number of experiments using diverse solvents, different quantities of acetic acid and at a variety of temperatures, had been carried out.

2. Table 10 lists the different olefins regenerated from their adducts by this method, the percentage yields, the means of estimation and of identification used.

3. The adducts(29) of cis-(85) and trans-stilbene(28) were regenerated and the olefins recovered had the same stereochemistry as the initial olefins. This was checked by g.l.c. on a 0.5% Apiezon L column at 50° and by infrared spectroscopy.

4. Treatment with copper had no effect.

5. The regenerations from the cyclohexene(71) and cycloheptene(73) adducts, were rapid exothermic reactions and the olefin boiled off unless the acetic acid (2ml.) diluted with ethanol (30ml.) was slowly added.

2-Chlorocyclohexyl 2,4-dinitrobenzene sulphoxide and sulphone.

The cyclohexene adduct(71) (0.5g.) was dissolved in glacial acetic acid (2ml.) and hydrogen peroxide (0.6ml.) added. The solution was heated on a steam bath for half

an hour, then allowed to stand at room temperature for twenty-four hours. The reaction mixture was diluted with ice-water (10ml.), the solid collected by filtration and washed with more ice-water. T.l.c. in 50% methylene chloride - 50% light petroleum showed two compounds of Rf - 0.23 and 0.43. These were separated by preparative t.l.c. in 80% methylene chloride - 20% light petroleum to give the sulphoxide(87) (0.22g.; 41%), d.p. 141 - 143° and the sulphone (86) (0.15g.; 28%), m.p. 130 - 131°. Spectral data is given in tables 11 - 14 and the chemical analysis in table 16.

2-Chlorocyclooctyl 2,4-dinitrobenzene sulphone.[53]

The cyclooctene adduct(74) (0.52g.) was treated as above but no solid obtained on dilution with ice-water so the reaction mixture was extracted with ethyl acetate (2x10ml.). The combined extracts were washed with ferrous sulphate, brine and sodium bicarbonate, dried over magnesium sulphate and the solvent evaporated. T.l.c. of the residual oil in 80% methylene chloride - 20% light petroleum showed many products present, none of which were predominant or could be isolated. The experiment was repeated and the progress followed by t.l.c. but no point was reached where either the sulphoxide or the sulphone were predominant.

TABLE 16

SULPHOXIDES AND SULPHONES.

Compound	M. p. °C	Yield %[a]	Microanalysis					
			Found			Calculated		
			C	H	N	C	H	N
86	130 - 131	86	41.43	3.75	8.23	41.32	3.75	8.03
87	141 - 143[b]	89	43.41	3.94	8.26	43.31	3.94	8.42
88	91 - 92	80	39.40	3.32	8.25	39.37	3.31	8.36
89	112 - 113	24	42.93	4.15	7.89	43.03	4.16	7.72
90	203 - 204	38	43.05	4.18	7.79	43.03	4.16	7.72
91	169 - 170	23	44.40	4.41	7.22	44.62	4.54	7.43
92	159 - 160[b]	62	46.45	4.47	7.71	46.60	4.75	7.76

a. Yields recorded are those of pure products obtained.

b. Decomposition point.

2-Chlorocyclohexyl 2,4-dinitrobenzene sulphoxide.[61]

The cyclohexene adduct(71) (0.37g.) was dissolved in acetic acid (6ml.), one equivalent of 30% hydrogen peroxide (0.14ml.) added and the solution heated on a steam bath for fifteen minutes. The solution was diluted with water (20ml.) and extracted with methylene chloride (2×15ml.). The combined extracts were washed with brine, ferrous sulphate and sodium bicarbonate, dried over magnesium sulphate and the solvent removed. The resultant solid was shown to be the sulphoxide(87) by comparative t.l.c.. Recrystallisation from methanol gave pure sulphoxide(87) (0.35g.; 89%), d.p. 141 - 143°.

2-Chlorocyclohexyl 2,4-dinitrobenzene sulphone.[61]

The cyclohexene adduct(71) (0.37g.) was dissolved in acetic acid (5ml.), two equivalents of 30% hydrogen peroxide (0.28ml.) added and the solution heated on a steam bath for one hour, by which time all the adduct had been converted to sulphone(86) (t.l.c.). The solution was diluted with crushed ice, the resultant solid collected and recrystallised from methanol to give the sulphone(86) (0.35g.; 86%), m.p. 130 - 131°.

Note

The above method of preparation of sulphoxides and sulphones

was repeated in exactly the same manner for the 1-(47) and 3-methylcyclohexenes(55), 1-methylcyclopentene(48), indene (44) and cyclooctene(74) adducts but multiple products were obtained in each case and only occasionally could low yields of the desired products be isolated.

2-Chlorocyclopentyl 2,4-dinitrobenzene sulphone.

The cyclopentene adduct(45) (0.21g.) was dissolved in acetic acid (7ml.) and a solution of potassium permanganate (0.25g.) in water (20ml.) added. The reaction mixture stood at room temperature for two hours with occasional shaking, then was decolourised with sulphur dioxide. Crushed ice (10g.) was added and the solid collected and recrystallised from methanol to give 2-chlorocyclopentyl 2,4-dinitrobenzene sulphone(88) (0.185g.; 80%), m.p. 91 - 92 . The spectral data is listed in tables 11 - 14 and the chemical analysis in table 16.

Note

The adducts of cyclooctene(74), 1-(47) and 3-methylcyclohexenes(55) were treated in the same manner except that they had to be heated for half an hour. The crystalline products were a mixture of sulphoxide and sulphone which were separated by preparative t.l.c. in 80% methylene chloride - 20% light petroleum. The results are shown in table 16.

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